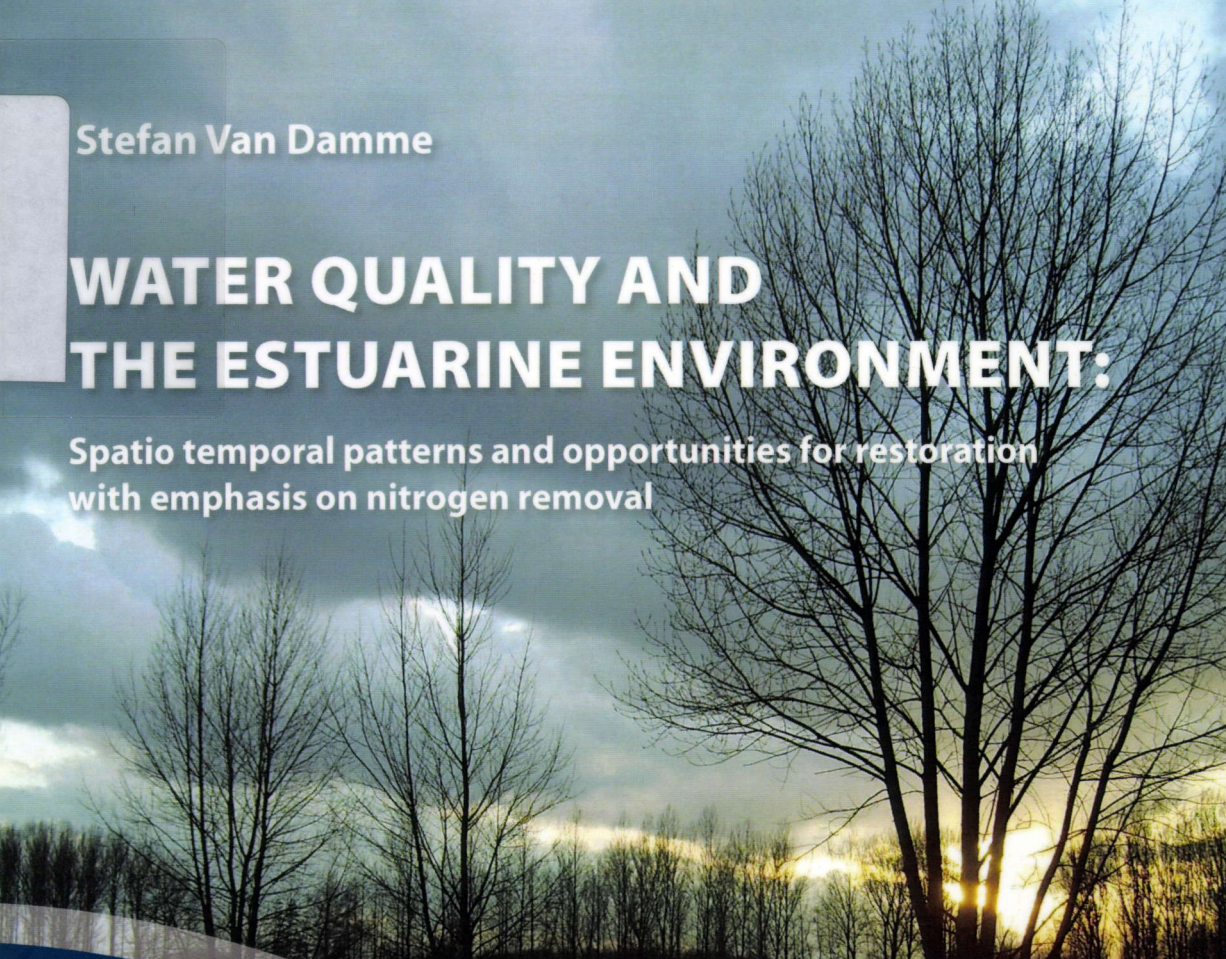
Stefan Van Damme

WATER QUALITY AND THE ESTUARINE ENVIRONMENT:

Spatio temporal patterns and opportunities for restoration with emphasis on nitrogen removal



Universiteit Antwerpen
Faculteit Wetenschappen
Departement Biologie
Onderzoeksgroep Ecosysteembeheer

WATERKWALITEIT EN HET ESTUARIEN MILIEU:

Spatio-temporele patronen en mogelijkheden tot herstel met speciale aandacht voor stikstofverwijdering

Proefschrift voorgedragen tot het behalen van de graad van doctor in de Wetenschappen verdedigd door Stefan Van Damme

Antwerpen, 2010

Promotor: Prof. Dr. Patrick Meire
Co-promotor: Prof. Dr. ir. Oswald Van Cleemput

Universiteit Antwerpen
ECOSYSTEM MANAGEMENT RESEARCH GROUP
UPA
University Press Antwerp

Universiteit Antwerpen
Faculteit Wetenschappen
Departement Biologie
Onderzoeksgroep Ecosysteembeheer

Water quality and the estuarine environment: Spatio temporal patterns and opportunities for restoration with emphasis on nitrogen removal

Waterkwaliteit en het estuarien milieu: Spatio-temporele patronen en mogelijkheden tot herstel met speciale aandacht voor stikstofverwijdering

Proefschrift voorgedragen tot het behalen
van de graad van doctor in de Wetenschappen
verdedigd door Stefan Van Damme

Antwerpen, 2010

Promotor: Prof. Dr. Patrick Meire
Co-promotor: Prof. Dr. ir. Oswald Van Cleemput

Print: Silhouet, Maldegem

2010 Uitgeverij UPA University Press Antwerp
UPA is an imprint of ASP nv (Academic and Scientific Publishers nv)
Ravensteingalerij 28
B-1000 Brussels
Tel. + 32 (0)2 289 26 50
Fax + 32 (0)2 289 26 59
E-mail: info@aspeditions.be
www.upa-editions.be

ISBN 978 90 5487 760 8
NUR 907 / 943 / 944
Legal Deposit D/2010/11.161/084

dan is het of de rivier, de weiden en de bomen nieuw zijn voor mij
want zij komen uit de wereld waarin ik de avond tevoren
met mijn gedachten heb geleefd.

Filip de Pillecyn

Dankwoord

In 1919 zaten de Britse troepen, die aan de kust van de Kaspische Zee de oliereserves van Baku moesten bewaken, een tijdlang zonder bevoorrading. Hun proviand was quasi op, toen een officier de lokale aanvoer van kaviaar in beslag nam. Het luxeproduct was in overvloedige hoeveelheden beschikbaar. Een soldaat kloeg in een brief naar huis: "Moeder, ze doen ons confituur eten van vis".
Net zoals kaviaar voor veeleisende fijnproevers heeft een doctoraat een exclusief kwaliteitskarakter. Een veelheid aan prioriteiten heeft mij de ampleur van het begrip 'doctoraat' echter vaak uit het oog doen verliezen, zodat het nogal eens ondankbaar en onterecht terzijde werd geschoven. Dit realiseer ik mij nu. Gelukkig stonden vele wijze mensen naast mij, om mij op de juiste weg te houden, en de erkentelijkheid aan deze geestelijke rijkdom wou ik hier graag uiten.

Het begon als een donderpreek bij heldere hemel. Prof. Patrick Meire, toen nog gewoon Patrick de Verschrikkelijke, stond en staat nog steeds voor inzet en compromisloze kwaliteit. Stap voor stap in de goede richting, is een van zijn deviezen. Met een visie die dermate ver strekt, is dat een boel stappen, een heuse levensweg. Maar telkens als we op een avond bij hem thuis het onderzoek bespraken, kwam ik buiten met zevenmijlslaarzen, richting essentie. Omdat hij zijn visie kan loodsen doorheen een poel van beslommeringen, expertise weet vast te houden in een duiventilsysteem, omwille van de wijze waarop hij zijn leerlingen emmers leert dragen naar een betere toekomst, verdient hij uiterste waardering.
Dank aan Dinska voor het onthaal en aan die 3 schalkse bengels voor de olijke momenten.
Dit onderzoek is geboren als onderdeel van het OMES programma, gekoesterd geesteskind van Patrick. Dergelijk programma was ongewoon qua omvang. Aan de wieg van het succes stond ondermeer Toon Tessier als padbeëffenaar. Financiering van mijn luik volgde vlak voor mijn huwelijk, eerst door VMM (met fijne herinnering aan Dhr. Henk Meackelberghe, Dhr. Martin Verdievel en later ook Mevr. Gaby Verhaegen en Mevr. Sandra De Smet), later door Afdeling Zeeschelde, thans W&Z (met bijzondere dank aan Dhr. Leo Meyvis en Dhr. Wim Dauwe). Ik dank Dhr. ir. Eric Taverniers voor het mogelijk maken van de vaarprogramma's. Dank aan alle scheepsbemanningen: van de MS Veremans, MS Scaldis I en de MS Scheldewacht. Bijzondere dank aan Marc Wouters; mensen als hij maken het leven mooi.

Onder de kundige leiding van Prof. Oswald van Cleemput leerde ik greep krijgen op die lastige piepkenduik denitrificatiemicroben. Werken met gas en gaschromatografie was er een veelbeoefende stiel. Pascal, Annick, Eric, Rosa, Alex, Denis, Nicolas, Samater en zovele anderen, het waren zalige tijden.

In een pitstop aan de VUB, in de groep van Prof. Willy Baeyens en Prof. Frank Dehairs, leerde ik meer over koolstof, isotopen en het programma Surfer. Willy en Frank heb ik leren kennen als zorgzame en uiterst degelijke coaches, elk op hun manier. En ja, Liesbet, Sandra, Lulu, Loreto en Natacha: mijn Arnout, toen geboren, is nog steeds de knapste van het heelal en daarbuiten, uiteraard.

Et bien, on ne peut pas dire qu'on ne travaille pas chez les francophones! Het telegeleide ULB-meetstation te Sint-Anna was impressionant. Ik leerde er kwaliteit van data evalueren. Les frères Wollast, Michel Verbanck, Pierrot Vanderborght, Lei Chou, Didier Bajura, Michèle Loijens en vele anderen lieten een grote indruk na. Je suis honoré d'avoir fait connaissance avec Rita, l'aimable, la courageuse.

Toen landde ik terug bij Prof. Dr. Patrick Meire die toen pas aan de UA benoemd was. Onbegonnen werk om alle mensen van ECOBE de revu te laten passeren. Al die fantastische mensen, divers en bijzonder, geschraagd door de bijkomende steun van Rudy Van Diggelen en Eric de Deckere. Speciaal te vermelden zijn buddies Chris, David en later poulain Eric die algauw de schaduw zijner kiezelvlerken over mij heen liet scheren, de Tommen met hun onderlinge deep drill discussies, sterk stimulerende kerels die nog veel gaan bereiken, en de ontstuimige nieuwe garde met o.a. Floor, de inmiddels appelblauwzeeontgroende Sander, kornuiten Olivier, Johnny en zoveel andere enthousiastelingen. De schatten van het secretariaat, Magda op kop, rotsen in de branding.
Bijzondere dank aan Prof. Rudi baron Verheyen voor zijn lange inzet inzake de koppeling tussen wetenschap en beleid, op vlak van milieu en natuur.
Dank aan de mensen van het labo: Lieve en Eva. Tom Van der Spiet en Anne Cools brachten modernisering, een opwaardering van de normen en een andere wind. Mijn uurtjes als kwaliteitsverantwoordelijke in hun bijzijn zal ik koesteren. En dan het onvergetelijk postuur van Dimi, de fiere molenaar, afgetekend op het ponton van Rhodos met de oogst van de zijrivieren.

Ik dank iedereen die mij bijstond bij het werk, alle OMES partners, mensen die de 13-uursmetingen meemaakten en de monsternames en het gewarrel van slijk. Ik dank in het bijzonder Nico De Regge, de goeie bolster.
Kijk daar loopt een adelaar. De omstandigheden waarin de IHD tot stand kwamen waren legendarisch moeilijk. Het team dat toen in de bres stond weet wat het betekent om tij te keren. Frank Adriaenssen, Erica Van den Bergh, Lieven Nachtergale, jullie waren echte strijdmakkers.

Ik dank allen die dit werk hebben beoordeeld, gelezen en becommentarieerd. Het is voor juryleden niet evident om de nodige tijd uit te trekken. Ik apprecieer hun moeite en hun oordeel.

Ik gedenk mensen die zijn heengegaan en in verband stonden met dit werk: Dhr. Leo Meyvis, Prof. Roland Wollast, Prof. Michel Frankignoulle, en Dhr. Guido Kerkhofs, motorist van de MS Veremans en toonbeeld van beroepseer. Zij laten een diepe indruk na. Vrienden, heft het glas.

Moeder, vader, jullie opvoeding is van onschatbare waarde gebleken. Wees maar zeker dat ik dankbaar ben voor wie ik ben geworden. Jullie kozen 100% voor mij, altijd, in alle kansen. Dank, ook aan 'ominopi', voor de goede zorgen aan onze twee kadetjes. Zonder jullie liefdevolle opvang zouden we er niet geraken.

Het laatste woord is voor mijn knuffelnest. Vrouwlief, zoonlief, dochterlief. Zonder jullie is er niets, jullie zijn mijn geluk. Zo simpel kan het zijn, zo simpel als een zoentje op het kruintje van je hoofd. Sorry voor alle doctoraatsoverlast. Ik zal het nooit meer doen.

Table of Contents

Chapter 1

Introduction

Van Damme S.

1.1 Nitrogen

'Three teenagers from a butcher's household were admitted to hospital as emergency cases after eating sausages' (Bacon, 1997). This diagnostic record of an acute nitrogen intoxication incident illustrates two things. Problems with nitrogen were in the past considered as local, with respect mainly to human health. Secondly, public health was really not much endangered, with exception of some aberratic cases; the nitrate issue concerned mainly potential risks and moderate effects rather than true hazards. The first European Directive (Drinking Water Directive 80/788) with regard to nitrogen confinement was intended to reduce possible health risks such as methaemoglobinanemia (blue baby syndrome), stomach- and other forms of cancer that could be linked with nitrate or nitrite.

Meanwhile, the main industrial process of producing N-fertiliser, using the Haber process in which atmospheric nitrogen is, under high pressure and temperature and in the presence of a catalyst, transformed into ammonia and then into ammonium, continued in ever greater quantities to fix nitrogen from the air into eventual release in the terrestrial and aquatic compartment. Biological nitrogen fixation was enhanced through specific crop stimulation. Fossil fuel emmissions added to nitrogen precipitation. The EU Nitrate Directive (91/676) recognised the regional scale of the nitrogen problem and the role of excessive use of fertilisers by compelling nations to designate vulnerable zones.

Although denitrifying bacteria can reverse nitrogen fixation by transforming nitrate to atmosperic nitrogen, the progressive fixation, use and emission of nitrogen in various applications have lead to a consequent nitrogen enrichment of ecosystems. The nitrogen issue has reached the global scale, resulting in a tremendous increase of world food production, hence public health benefit, since the 1960s. The trophic balance in many systems however shifted towards eutrophied, value poor dominance of pest species, bacteria, or even to anaerobic conditions. The ecosystem enrichment has been recognised by *e.g.* the EU Water Framework Directive (2000/60), demanding action for all water bodies. New negative feedbacks on direct health issues include an increase in respiratory ailments and allergies due to enhanced gaseous emissions, interaction of these emissions with ozone and increase of pollen production (Townsend *et al.*, 2003). Indirectly, vectors of infectious deseases have become more abundant, the risk of cholera outbreaks has increased in several countries, amongst other effects.

On a global scale, interactions between the nitrogen cycle, the carbon cycle and climate are now expected to become increasingly important up to the brink to become a determinant of the Earth system (Gruber & Galloway, 2008).

Arguments for the need to control nitrogen have evolved over decades. The need for control has remained predominant. This thesis intends to give a contribution to the knowledge on nitrogen reduction.

In the sense of this evolution of the nitrogen issue, apart from the decision supporting advice that is intended in this script, it might be nice indeed, thinking about Bacon (1997) especially from wider perspectives, to ingest one sausage less.

1.2 Estuaries

Long ago, many large and important cities (*e.g.* Hamburg, Washington, Philadelphia, Rotterdam, Bordeaux) were established in the freshwater tidal zone of estuaries, in part because it was the most inland point that could be reached by ships. Estuaries were ideal, sheltered locations for the establishment of international trade and economic hubs (Baldwin *et al.*, 2009). As societies and human welfare developped, the demand for more supplies and trade, hence ship dimensions, grew accordingly. Deeper fairways were needed. Especially if the estuarine mouth is funnel shaped, which is very often the case, a deepening of the system results in tide amplification. Land reclamation is thought to have had in many cases a

stronger impact on tide amplification than deepening fairways. The sheltering aspect of the port cities, from where so much of trade and commerce started, has globally changed: the shelter against the surf still persists, but the increasing tide wave caused concern. In many estuaries (*e.g.* the Ems, the Elbe, the Scheldt), an increase in land reclamation and port accessibility is parallelled by a growing need for safety against floods.

From ecological point of view, estuaries are valuable as well. Likewise as for human trade, they are unique sea-river corridors: Various life forms need estuaries to migrate from marine to fresh water habitats or vice versa. Numerous birds migrate along north-south axes following estuarine habitats. Many species need estuaries for shelter, as nursery room, spawning grounds, feeding grounds, resting sites or as permanent living habitat. The productivity to host all this life originates from the fact that estuaries receive the input from the whole adjacent river catchment. Nutrients, organic matter and suspended sediments have, relative to other aquatic ecosystems, always been amply available in estuaries.

Estuarine habitats have witnessed a long history of degradation. Land winning, fairway deepening, increasing emissions have all had their impact on habitat quantity and quality (Meire *et al.*, 2005). Awareness of habitat loss was on a european scale first recognised in the European Bird Directive (79/409) (*i.e.* 1 year before the Drinking Water Directive; Fig. 1.1).

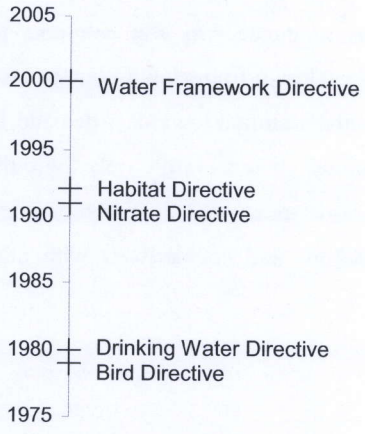


Fig. 1.1: Timeline of European Directives related to this work

This directive requires the conservation of all natural wild living bird species on the territory of the member states. As the creation of local Bird Directive areas is not meant to mitigate the overall ecological condition of estuaries, other measures were needed.

The Habitat Directive (92/43) introduced the concept of Conservation Objectives. These objectives have to be constructed in such way that the habitats and the species they contain are self sustainable in the long term. The objectives can be constructed as wide and as profound as necessary. Habitat Directive areas have been designated, including in estuarine environments, on which the Conservation Objectives must be applied. Within estuaries, intertidal areas are predominant habitats, as they provide unique communities and high production. Creating Conservation Objectives in a quantified way has however shown to be very difficult, as there is even nowadays, after almost 20 years, still need of quantified manageable objectives.

The Water Framework Directive (2000/60) shows the clearest convergence between the nitrogen problem and estuarine ecological recovery in a broader sense, in stating that a good ecological status has to be achieved on the chemical, fysico-chemical, biological and hydro-morphological levels. Nitrogen as key element of water quality and primary production played a central role in ecological restoration, as it was known to be the limiting element for aquatic primary production in the North Sea and (the marine part of) estuaries (Peeters & Peperzak, 1990).

The complex estuarine environment offers possibilities to create win win solutions for different problems. The legislative framework shows an evolution from single issue towards a more integrated vision. The need for knowledge essentially shifted towards a demand for system integrative overall comprising management solutions. It is therefore only logic that policy oriented science follows and/or anticipates the same trend, and that, if nitrogen is scoped in estuarine environments, also possible interactions and comparisons with other issues are explored.

1.3 Objectives

Although definitions for the word 'estuary' are manyfold (Elliott & McLusky, 2002), and various discordances about estuarine typology persist, one thing is, however, clear: Estuaries offer a last opportunity to manage waste load emissions before they become unmanageable in the coastal zone. This thesis links the nitrogen issue and the need for estuarine restoration.

Especially the role of benthic denitrification in intertidal sediments was a specific initial target.
The overall initial aim of this work was:

- to assess the potential of intertidal areas on nitrogen removal.

This was translated in the specific target to determine denitrification, its spatial and temporal variation and the explaining variables, in intertidal areas of the schelde estuary.
However, in the setup phase of the study it became soon clear that the freshwater tidal zone of the Schelde was from a general scientific point of view *terra incognita*. Monitoring of the water column was scattered and scarce (Van Damme *et al.*, 1995), as this part of the estuary was considered as 'river' rather than as 'estuary'. This lead to another objective:

- to characterise the water quality and nitrogen issue for the freshwater part of the Schelde estuary.

This was translated in the specific target to sep up an estuarine monitoring including the fresh water tidal zone, and to centralise the ecological knowledge of fresh water tidal zones.
Linking the obligations of the different Directives leads to a third objective:

- to integrate knowledge on water quality and nitrogen into quantified restoration opportunities and needs for the Schelde estuary.

This objective gained importance during the course of this thesis, as monitored nutrient ratios (Soetaert *et al.*, 2006) and model results (Billen *et al.*, 2005) indicated that nitrogen was no longer the limiting nutrient for primary production in the estuary. Instead of deeper investigating the denitrification process the choice was made to widen the subject towards comparitive and integrative research.

1.4 This work

After the general introduction, objectives and outline of the thesis (**Chapter 1**), a literature study is presented, assembling the existing knowledge of freshwater tidal zones around the

world (**Chapter 2**). One of the key products of eutrophication is excess algal growth. Aquatic primary production is the main scope of this synthesis as a center point of ecological functioning and nutrient enrichment.

At the onset of this study, basic data on water quality were partly lacking. **Chapter 3** shows the monitoring data of the Belgian part of the Schelde estuary, the Zeeschelde, - gathered during this thesis - linked with results of the Dutch part, called Westerschelde. This offered for the first time a monitoring view of the whole estuary.

Concentrations offer a less thorough insight into eutrophication than loads. In **Chapter 4**, the water quality monitoring data are further analysed, including the effect of discharge.

Chapter 5 focusses upon denitrification in mudflats, as measured with the acetylene technique. N_2O emission is also scoped, and is compared with the emissions of other greenhouse gases.

Chapter 6 focusses upon a freshwater tidal marsh. A watercolumn – marsh exchange budget presents the nitrogen retention of the marsh among many other parameters. A ranking of retention and release is presented for nutrients, oxygen, suspended matter and other parameters in order to have a first idea about the relative importance of different ecological functions of a tidal marsh.

Chapter 7 integrates all gathered knowledge into a quantification tool for mudflat area needs on a system scale. Water quality data, modelling and trophic relations are combined with area evolution and diversity restrictions into comparative scenarios of benthic faunal production. It is the aim not only to present water quality requirements, but also to translate the comparative scenarios into quantified habitat area compensation needs.

Chapter 8 presents a synthesis of this thesis, offering also a view on the impact of this study on management of the Schelde and other estuaries.

A summary in Dutch is provided in **Chapter 9**.

Chapter 2

Characteristic aspects of the tidal freshwater zone that affect aquatic primary production

Van Damme S., Struyf E., Maris T., Cox T. & Meire P.

Barendregt A., Whigham D.F., Baldwin A.H. (Eds) Tidal freshwater wetlands. Backhuys Publishers, Leiden, The Netherlands, pp. 123-136.

Abstract

Aquatic-based processes have not been well studied in tidal freshwater habitats even though they are diverse and highly variable systems. This chapter aims at a synthesis of the state of knowledge about aquatic primary production in tidal freshwater ecosystems and the main factors that control this process. Suspended matter is important in tidal freshwater habitats and it is affected by estuarine processes as well as land use and river discharge into the tidal freshwater zone from the catchment area. As a result, variation in the amount and quality of suspended matter influences the variability of light availability. The retention and transformation of nitrogen and phosphorus in the tidal freshwater zone is often intense and wetland vegetation has a major impact on the silica cycle within the tidal freshwater zone of estuaries. Although the primary producers follow a constantly changing equilibrium that is influenced by tide action and river discharge, they show characteristics that contrast with general ideas about primary producers in estuaries. The scarceness of data, together with weaknesses in methodology to measure or model primary production, is however in striking contrast with the complexity and importance of these neglected ecosystems. Nevertheless, within the tidal freshwater zone of the Scheldt estuary, two types of phytoplankton communities have been recorded, indicating that a typology for freshwater tidal systems is waiting to be revealed, taking into account *e.g.* residence time. The dynamic nature of tidal freshwater habitats implies that static, site-bound legislative protection measures tend to be less efficient than a functional approach. Comparative estuarine research offers a good

opportunity to expand our knowledge about the ecological functioning of these important estuarine systems. As an example it is demonstrated here that it is possible to estimate historic suspended matter concentrations.

2.1 Introduction

Tidal freshwater wetlands (hereafter called TFW) were first brought into scientific attention because of their peculiar ecological characteristics (Odum, 1988). In contrast with most estuarine habitats, the tidal freshwater zones have long been regarded as riverine stretches. Consequently, few estuarine ecologists had studied TFW habitats. Probably the first attempt to bring together information on the tidal freshwater region of estuaries in Europe was an ECSA (Estuarine and Coastal Sciences Association) symposium (Meire & Vincx, 1993) held in Gent, Belgium in 1991 (Elliott & McLusky 2002). At that time, tidal freshwater reaches were considered to be specific entities with a combination of riverine and estuarine aspects (Schuchardt *et al.*, 1993). The tidal freshwater region was recognized as a zone which was different from riverine sites due to specific physical processes such as prolonged residence time of water, oscillating water levels, and changing current velocities and directions. All the papers presented at the Gent symposium demonstrated that the tidal freshwater region of estuaries experienced a great deal of natural stress, arising from characteristic chemical and physical processes. A seasonal and spatial oxygen sag is typical of tidal freshwater habitats, often associated with a turbidity maximum, and compounded in many cases by discharges of carbon and nutrients from human habitation (Eliott & McLusky 2002). Phytoplankton-based aquatic primary production in tidal freshwater habitats received little attention, despite its presumed key position in aquatic food webs as well as its importance in ecological functioning.

It was observed that phytoplankton composition and densities were different in TFW compared to phytoplankton communities at the freshwater-saltwater interface or in the upstream (non-tidal) riverine systems (*e.g.* Jackson *et al.*, 1987; Schuchardt & Schirmer, 1991; Rehbehn *et al.*, 1993). Although the factors that determine phytoplankton production in general were already known such as nutrients, temperature, and light (*e.g.* Cloern, 1987), the rates of aquatic primary production, the effects of various factors on primary production, and the impact of primary production on the system were less clear. The importance of the role of autochthonous production in estuarine food chains has been more and more recognized. In contrast to prevailing ideas, the role of allochthonous detritus for the estuarine food chain has been questioned (*e.g.* Sobczak *et al.* 2005), while more evidence is found that aquatic primary production fuels the food web to a greater extent than had formerly been assumed. Even in TFW with overwhelming amounts of detrital carbon from a variety of sources, nutritional

factors associated with phytoplankton were found to be dominant in regulating zooplankton growth (Muller-Solger *et al.* 2002).

In this chapter, the status of aquatic primary production in the tidal freshwater region is reviewed with special emphasis on the factors that control productivity. Production rates and impacts of the production on the system are also evaluated. We begin with a synthesis of the factors influencing pelagic primary productivity. We then focus on the primary production rates and patterns.

2.2 Factors influencing phytoplankton production

Human activity in coastal catchments (*i.e.*, watersheds) greatly increased the fluxes of growth-limiting nutrients from the landscape to receiving waters. This has resulted in greatly increased nutrient concentrations in many of the world's estuaries (Verity, 2002) and coastal ecosystems (Cloern, 2001; Van Beusekom & De Jonge, 2002; Smith *et al.*, 2003). In clear waters, increases in nutrient loading caused predictable increases in the algal biomass (Borum & Sand-Jensen, 1996), sometimes leading to exceptional algal blooms (*e.g.* Richardson, 1997; Dippner, 1998), which may deplete water-column oxygen (Rabalais *et al.*, 1996). In addition, altered proportions between nutrients induce changes in the algal species composition (Officer & Ryther, 1980; Lancelot *et al.*, 1987) and food web structure (*e.g.* Escaravage & Prins, 2002). In contrast, in turbid waters, the effects of increased nutrient loading may not be as pronounced (Cloern, 2001). In these systems, phytoplankton production is often light-limited year-round, and growth is low despite the high levels of nutrient input (Heip *et al.*, 1995). The availability of light and nutrients are main factors that influence pelagic primary production.

2.2.1 Light availability

Light availability to pelagic primary producers of estuarine waters depends on both the mixing depth of the producers and the photic depth of the system (Grobbelaar, 1990). In well-mixed estuaries the mixing depth corresponds with local depth. Stratified estuaries usually are less dynamic than fully mixed ones. A comparative analysis of 26 microtidal (most of them in North America) and 14 macrotidal (mostly European) estuaries revealed that the macrotidal estuaries, which are characterized by high tidal energy, significantly exhibited lower levels of chlorophyll *a* than systems with lower tidal energy, even when nitrogen concentrations were

equal to or higher than in the microtidal systems (Monbet, 1992). This indicates that light conditions are predominantly limiting primary production in dynamic macrotidal and well-mixed estuaries, where the photic depth is determined by turbidity, as was shown in detail by Colijn *et al.* (1987). Therefore it is necessary to understand what determines turbidity in such estuaries and especially in their freshwater reaches.

Turbidity is a cloudiness or haziness of water caused by individual particles (suspended solids). Dissolved materials are not included in this definition, but they can also contribute to light attenuation. In oceans or stagnant waters, turbidity is generally caused by phytoplankton. Estuaries however, especially macrotidal systems (average tidal amplitude at least 2 m, see Elliott & McLusky 2002), are known for their high levels of turbidity, where some fish species are hidden from visual predators (Maes *et al.*, 1998). Indeed estuaries can trap sediments coming both from the saline estuary or from the freshwater catchment area, but local mixing also affects turbidity.

2.2.2 Turbidity at the downstream limits of the freshwater zone

In macrotidal estuaries, the freshwater-saltwater interface is often characterized by a strong estuarine turbidity maximum, of which the mechanisms have been investigated since Postma and Kalle (1955). Sometimes, the turbidity maximum may be independent of salinity, such as in the Tay estuary, where wind-wave resuspension of sediments in shallow water and ebb tide transport to deeper channels keep the turbidity maximum in a longitudinally fixed location (Weir & McManus, 1987). Most often, turbidity maximum can be found where saline water intrudes into the estuary along the bottom, under a layer of less heavy freshwater, thus forming a typical salt wedge. The tip of this salt wedge is in many estuaries the place where this turbidity maximum is most pronounced (*e.g.* Postma & Kalle, 1955; Salomons *et al.*, 1988; Uncles & Stevens, 1993).

2.2.2.1 Mechanisms

Three processes explain the turbidity maximum at the freshwater-saltwater interface: residual gravitational circulation, tidal velocity asymmetry, and tidal mixing asymmetry. The importance of each of these mechanisms varies and is subject of discussion. The residual gravitational circulation is caused by a baroclinic, density driven pressure gradient. This pressure forces the near-bottom horizontal velocity upstream where it meets the freshwater flow going downstream. If the pressure gradient is strong enough, the resulting flow shows a

gravitational circulation within the vertical plane. This mechanism stands apart from tidal action and it can dominate in microtidal estuaries or where topographic depth profiles show major changes (*e.g.* Schubel & Carter, 1984). The tidal velocity asymmetry is, *e.g.* in the Elbe (Burchard & Baumert, 1998), a much more important process causing a turbidity maximum. Due to the convective instability of the near-bottom flow at flood tide, the vertical velocity profile is much more uniform at flood than at ebb tide. As a consequence, velocity profiles are bottom-intensified during flood and surface-intensified during ebb. As the suspended matter concentrations (SPM) are usually higher toward the bottom, this asymmetry in flow patterns can lead to upstream net transport of SPM. The third mechanism, tidal mixing asymmetry, originates from the stable stratification of the ebb current (faster flowing freshwater at the surface moves over slower moving salty layers at the bottom). At the resulting density interface, vertical mixing is suppressed such that almost all SPM is kept below that interface in the region of slow velocities. The consequence is again net upstream SPM transport. These processes result in a residual near-bottom upstream current that traps SPM. If either the residual gravitational circulation or the tidal velocity asymmetry would be reduced, then the turbidity maximum would weaken or even vanish (Burchard & Baumert, 1998).

On top of and combined with these turbidity-generating mechanisms, another sediment-based process is important. Since Eisma (1986) the cohesive behavior of sediment (clay, silt and sometimes fine sand) and organic matter (debris or even living bacteria), clustering together to form porous flocs of varying size and composition, a process known as flocculation, has received increasing interest. In low energy conditions at low SPM concentrations, such as in many rivers and small microtidal estuaries, floc size and composition are rather constant, as the flocculation time is relatively large (Winterwerp *et al.*, 2006). On the contrary, in high energy conditions at high SPM concentrations, as met in many macrotidal or large estuaries, variation is huge. A conceptual diagram, suggesting that floc size changes with SPM values and turbulence shear (Fig. 2.1), is, without disregarding the gained knowledge on the role of ionic strength, still used as a basis for further research into the causes and characteristics of flocculation (Winterwerp *et al.*, 2006).

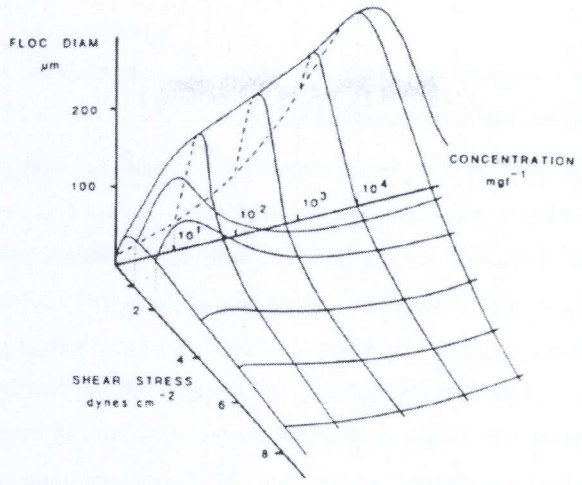


Fig. 2.1: Diagram showing floc diameter as a function of shear stress and suspended matter concentration. Source: (Dyer, 1989)

2.2.2.2 Variation

Although the residual current is quite stable on a long-term multi-tidal cycle scale, especially when the bottom topography enhances salinity stratification, short-term variation in the location and characteristics of the turbidity maximum can be considerable due to changes in gravitational circulation and turbidity maximum formation in general (*e.g.* Schoellhamer, 2001). Thus, migration distances of a turbidity maximum within an estuary can be considerable. When the tidal range increases in the neap-spring cycle, the high current velocities required to make resuspension of deposited SPM are sustained for longer periods. For instance in the lower Forth estuary an increase of tidal range from 4.0 to 4.8 m resulted in an increase of an order of magnitude in net landward sediment transport (Lindsay *et al.*, 1996). This illustrates that spring cycles can be of dominating influence in sediment transport. At spring tide the turbidity maximum, fed by strong upwelling, can migrate upwards of the freshwater-saltwater interface and enter the freshwater zone, as has been described, *e.g.* for the Tamar estuary (Uncles & Stevens, 1993).

Concerning spatial variation, it has been shown that shallow areas tend to be more flood-dominated than deeper areas (Wang *et al.*, 2002), so that the shallow areas are more prone to upwelling by the stronger flood currents. For pelagic primary production, a favorable mixing depth does not necessarily go hand in hand with an optimal photic depth, although sediment-dwelling algae can be important primary producers (V. de Jonge pers. comm.).

2.2.2.3 *Combining comparative estuarine research and historic reconstruction: an opportunity for light environment assessment*

Although there is a reasonable understanding of the spatial variation and mechanisms of turbidity, and of its short-term variation, the long-term evolution of turbidity patterns is, however, less clear. Estuaries are naturally in constant evolution, and it is difficult to determine trends of the light environment. Succeeding in this reconstruction is very important, however, for instance in constructing reference conditions for estuarine primary production, the basis of the food web. Linking turbidity with morphological and hydrological aspects provides some opportunities. Using consistently derived data from 44 estuaries in Europe and the Americas in an inter-estuarine comparison, SPM concentrations were shown to be significantly related to tidal intrusion length, tidal range, and residence time (Uncles *et al.*, 2002). Longer estuaries generate faster tidal currents for a given tidal range at their mouth and, in the presence of a supply of erodible fine sediment, therefore produce greater concentrations of suspended matter that can accumulate in turbidity maximum zones. The same is true if the tidal range is increased for estuaries with a given length (the inter-estuarine relation between SPM, mean tidal spring range, and tidal intrusion length could explain 74% of the variation). Thus, a large microtidal estuary can be as turbid as a small macrotidal estuary (*e.g.* Chesapeake Bay compared to the small Yeo estuary). It also explains exceptions in the comparative study by Monbet (1992), *e.g.* why in the microtidal but very long Hudson River estuary high nutrient concentrations do not give rise to high chlorophyll values. These relations can be applied to reconstruct historic SPM concentrations, if the temporal development of the determining parameters is known.

For the heavily impacted Scheldt estuary such results are available. Documentation of the morphology of the Scheldt in 1650, 1800, and 1968 AD (Coen, 1988) provided information that Van der Spek (1997) needed to develop a hydrological reconstruction of the tidal characteristics. The evolution of the tidal range of the Scheldt estuary (Fig. 2.2a), applied to Uncles *et al.* (2002) (Fig. 2.2b) indicated—although with a large degree of error due to the log-log-transformed axes on a smoothed kriging surface plot—that the SPM concentration at the mouth in 1650, was only about one third to one quarter to what it is at present. It seems logical that further upstream, the difference between the historic situations must have been even larger, as the tidal range is amplified closer to the upper limits of tidal influence (Fig. 2a). Although this is only a rough estimate, not taking into account *e.g.* the evolution of the

tidal intrusion length, it is nevertheless a strong indication that the light environment in the Scheldt estuary was indeed negatively affected by large-scale embankments between 1650 and 1968.

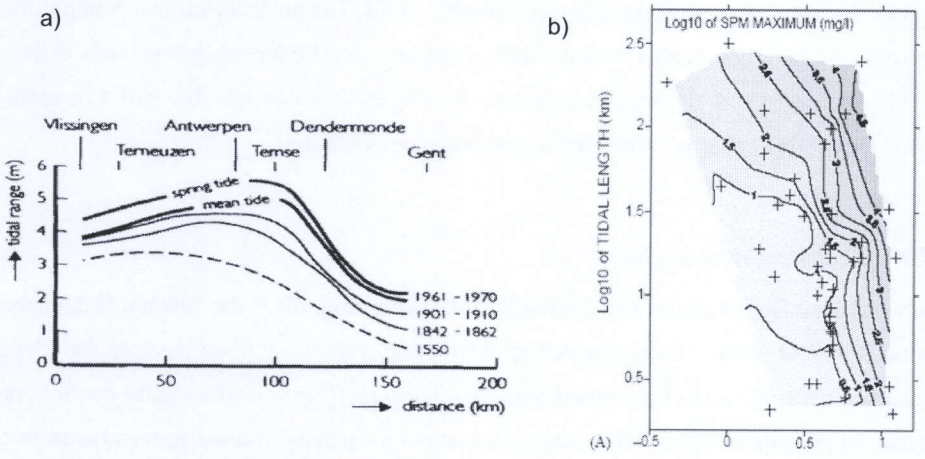


Fig. 2.2: Combining historic reconstruction and estuarine comparative results: a) Reconstruction of the variation in mean tidal range along the Scheldt estuary (Source: Van der Spek 1997); b) Estuarine suspended matter (SPM) maxima as a function of tidal length and mean spring tidal range at the estuarine mouths. Source: (Uncles *et al.*, 2002)

2.2.3 Turbidity in the freshwater zone

2.2.3.1 Tidal influence

As the tidal wave progresses through an estuary farther inland, it becomes increasingly reflected against the shoreline, and hence distorted. The steeper water level gradient during the short flood tide phase causes larger maximum current velocities during the flood than during the longer ebb phase. In TFW zone this tidal asymmetry reaches its maximum (*e.g.* Meire *et al.*, 2005). As a result the residual sediment transport of this mechanism, called tidal pumping, is directed upstream, contributing to the existence of the turbidity maxima in TFW zone (*e.g.* Salomons *et al.*, 1988; Grabemann & Krause 2001). Sediment transport is exponentially proportional to current velocity, which strongly amplifies the inequality between flood and ebb transport.

When indications are available that, by a specific length-depth relation of an estuary, the lateral and upper boundary reflections of the initial tidal wave can give rise to resonant behavior, the reflection of the tide that case gives rise to a pattern of standing waves. This

pattern can be recognized by observations that the height of the tidal wave is constant over a large longitudinal distance. Standing waves can dominate as an organizing mechanism for sustaining turbidity maxima (Rolinski & Eichweber, 2000). This is likely the case in the Elbe estuary, where three different turbidity maxima upstream of the salt wedge were simulated under low discharge and wind conditions (Rolinski, 1999). The nodes of idealized amplitudes of over-tide velocities coincided with the main dredging sites. Sedimentation prevails at these sites. This indicates that, if resonance occurs, it can provoke considerable shifts in spatial patterns of estuarine ecology, compared to non-resonant conditions.

2.2.3.2 Influence of river discharge

The immediate effect of freshwater discharge on the incoming tide is dampening. If discharge increases, the tidal wave—in the absence of obstructing sluices—will not reach as far inland, also causing shifts in tidal characteristics so that discharge from a certain point controls the amplitude of the tide (Godin, 1999), and tidal pumping weakens. But discharge also imports material from the catchment area. According to a model that calculates erosion and sediment transport from land to water bodies (Van Oost *et al.*, 2000; Van Rompaey *et al.*, 2001), the load of sediment entering the streams of the Scheldt catchment is nearly completely induced by human impact. Erosion of arable land clearly was the dominant factor. This eroded material eventually reaches the estuary, whereby the river discharge determines the imported load as well as the residence time in the system. From 1996 to 2000, a period in which the yearly discharge of the Scheldt gradually more than doubled, the suspended matter load discharged into the estuary more than tripled (Struyf *et al.*, 2004). It was demonstrated that the concentrations of SPM increase with increasing discharge (Vanderweijden & Middelburg, 1989). In the Tweed River, a small meso-tidal estuary with low turbidity, 80% of the variance of freshwater turbidity was explained by discharge of the inflow, which had occurred 30 hr earlier (Uncles & Stevens, 1997). This time lag between turbidity and inflow is a feature of fluvial systems, and is likely to increase if the surface of the drainage basin is larger. Generally, the SPM in the TFW has a finer texture than its marine counterpart (*e.g.* Uncles & Stevens, 1997; Chen *et al.*, 2005). Within the TFW, flocculation has been studied much less than in the turbidity maximum at the freshwater-saltwater interface. In the Scheldt estuary, it was observed that the average floc size increased with decreasing salinity with maximum size occurring well within the TFW (Chen *et al.*, 2005). The availability of dominating quantities of small size individual sediment particles and a high concentration of organic matter,

together with reduced energetic conditions relative to the freshwater-saltwater interface, may explain this observation.

SPM of the TFW zone is usually rich in organic matter. In the Scheldt estuary, a combination of isotope and budget studies indicated that up to one quarter of the SPM could consist of anthropogenic organic matter, *i.e.* during the winter (Van Damme *et al.*, 2005). In summer, anthropogenic organic matter was as high as 10%. This indicated that the implementation of wastewater treatment can attribute slightly but directly to the improvement of light conditions for pelagic primary production in the TFW. In the brackish part of the Scheldt, organic matter is already degraded to such an extent that this factor is of no importance anymore.

The combination of tide and discharge, under normal discharge conditions, causes a specific springtide-neap tide pattern (Fig. 2.3). During spring tides, the flow of river water masses and the transport of suspended particles from the freshwater zone to the brackish and marine zone are slowed due to the increase in estuary water volume (Guézennec *et al.*, 1999). Concurrent with this spring tide phenomenon, strong tidal currents generate maximum suspended load concentrations, so that the tidal pumping can even stop the net downward sediment transport.

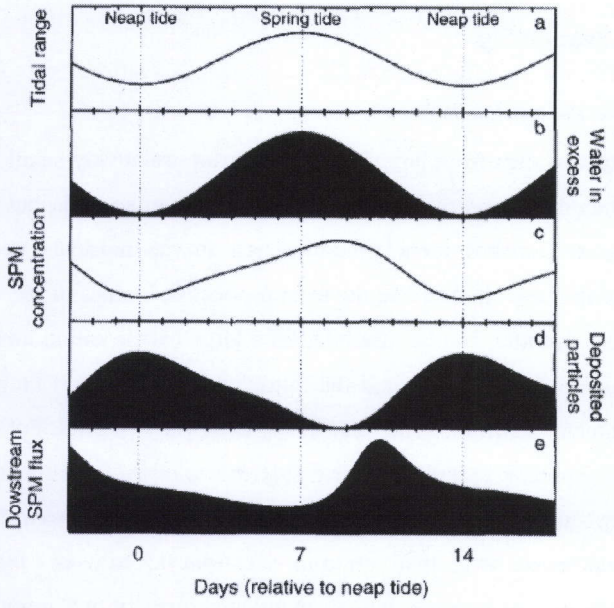


Fig.2.3: Conceptual sketch of particulate transfer during spring-neap periods onto the upper Seine estuary. Downstream suspended matter flux is maximum during the spring-neap tide transition. Source: (Guézennec *et al.*, 1999)

At the end of the spring tide period, when the SPM concentration is at its springtide-neap tide peak and the low tide level drops, the transport of SPM downstream reaches its maximum. This period is of short duration, as sedimentation prevails during neap tides.

Extreme river discharges, however, cause a dispersal of SPM from the turbidity maximum to a location further downstream. If this dispersal reaches the sea, then the estuary is flushed substantially and the water is temporarily much clearer. Whereas salinity responds relatively rapidly to changes in runoff, *e.g.* in the Weser and the Tamar estuary within days or even hours (Grabemann *et al.*, 1997), reestablishment of the turbidity maximum after a river spate can require weeks or even months. For the Seine it has been shown that human impact, resulting in a reduction of estuarine space, shifted the main deposition zone of mud brought by winter floods all the way down to the open marine zone, where sandy zones received increasing quantities of silt (Lesourd *et al.*, 2001). The threshold circumstances between net filling or emptying of the TFW by SPM need further integration, but this requires not only a well described relation between turbidity and hydraulic morphology characteristics such as residence time and tidal asymmetry, but, simultaneously, a quantified relation between sediment input in the estuary, discharge, and land use in the catchment area.

2.2.4 Nutrient availability

2.2.4.1 Input from the catchment area

Estuaries concentrate waters from large land surfaces into relatively small water bodies. The constant replenishing of the supply of nutrients from mainly the river, but also directly from the land and the sea, makes them generally rich in the nutrients needed for primary production, and so they are cited among the most productive biomes of the world (Costanza *et al.*, 1997). Whereas turbidity can be generated to a large extent within estuaries, the relation between the estuarine water quality and the nutrients (N, P, and Si) they receive from the surrounding catchment is stricter, especially in the freshwater reaches. For instance, although the control of N export is complex, among-system variation for large rivers is predicted relatively well by simple models of human activity. Using data from 249 predominantly north-temperate catchment areas that varied in size from 0.1 to over 1,000,000 km^2, it was found that the relationship between human population density and nitrate export becomes weaker at smaller scales, and that for catchments less than 100 km^2, it explained only 8% of the 1000-fold variation in nitrate export into the estuary (Caraco *et al.*, 2003).

Growing awareness of the eutrophication problem in coastal zones, estuaries, and rivers has led worldwide to measures to reduce waste loads, such as the Clean Water Act in the USA in 1972 or the European Water Framework Directive (2000/60/EC). As a result, long-term trends of water quality have significantly improved for several estuaries, *e.g.* the Hudson (O'Shea & Brosnan, 2000), where untreated municipal waste loads were reduced from 197 m^3 s^{-1} in 1970 to 0.044 m^3 s^{-1} in 1993. In Europe, the Seine (Billen *et al.*, 2001), the Scheldt (Soetaert *et al.*, 2006) and the Elbe (A. Schoell pers. comm.) all improved from the mid-eighties until the present day. Chinese estuaries, in contrast, over the same period showed their worst decline in water quality ever, *e.g.* dissolved inorganic N concentrations increasing in the Yangtze from 100 to 300 μM and dissolved inorganic P from 25 to 150 μM, leading to a sharp decrease in macro-zoobenthos biomass and causing algal blooms in the adjacent sea (Wang, 2006).

However, a higher proportion of the nutrients loaded to the coastal zone flows through estuarine systems as compared to landscape features located higher in the catchment area. A small increase in the retention of nutrients in the TFW zone may therefore be far more important than a large retention in some buffer strip high up in the catchment, as was indicated for the Hudson (Lampman *et al.*, 1999). This explains the need for understanding nutrient cycling in TFW habitats.

The main regulator of nutrient input from the catchment area into the TFW is discharge. Flow variation can induce several major changes in estuarine water quality and in estuarine functioning. In the freshwater and brackish reaches of the Scheldt estuary, higher discharges apparently improved water quality by diluting nutrient concentrations (Struyf *et al.*, 2004). A positive effect on oxygen concentrations was shown at higher discharge. This masks a problem of increasing total loadings of nutrients. The effect of increasing discharge on the loads of ammonia, nitrate, and silica concentrations is opposite in spring and summer from autumn and winter (Fig. 2.4). With increasing discharge, summer concentrations of dissolved Si (DSi) increased to the level of winter concentrations, indicating reduced consumption of DSi, probably through washout of the diatom community. If future global change would lead to higher discharge, this could flatten out the seasonal cycles for nutrients. The relevance of this phenomenon depends on the importance of the pelagic processes.

2.2.4.2 Pelagic processes

TFW are usually more turbid than their upstream riverine counterparts (M. Lionard pers. comm.). The increased amount of SPM has been related to some changes in the pelagic processes. Ammonium-oxidizing, nitrifying bacteria are associated with suspended particles. These bacteria are chemoautotrophic and therefore must be included as important components of primary production; however, it is not the scope of this study to include chemoautotrophic primary production. It was shown for the river Seine that, while in the river ammonium was slowly nitrified, in the TFW zone, with its longer residence time, nitrification was rapid and complete (Brion *et al.*, 2000).

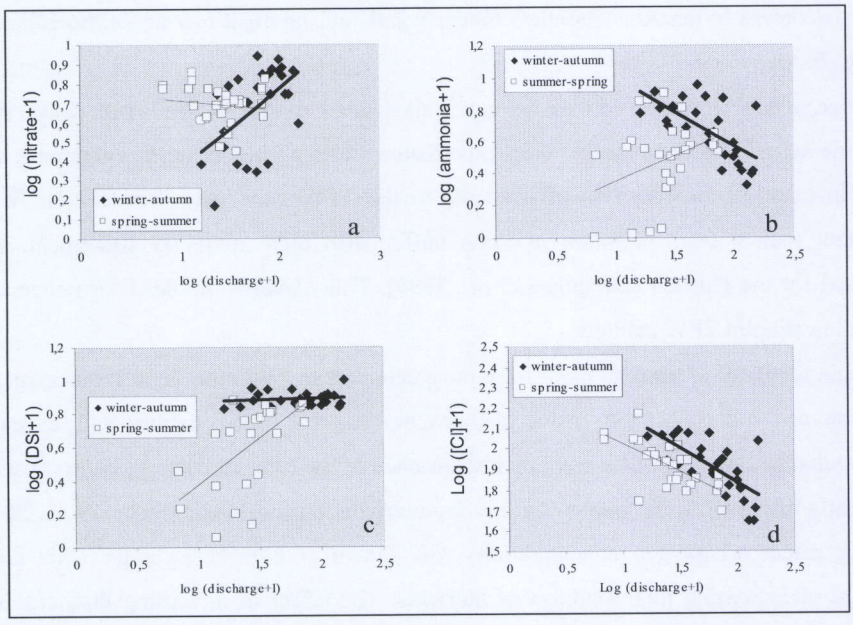


Fig. 2.4: Relation (least-squares linear regression) between total monthly discharge and monthly nutrient concentrations in spring-summer (April-September) and autumn-winter (October-March) in the tidal freshwater zone of the Scheldt estuary (Dendermonde). a) nitrate (summer-spring p=0.40, r^2=0.03; winter-autumn p=0.003, r^2=0.29) b) ammonia (summer-spring p=0.06, r^2 = 0.13, winter-autumn p=0.0001, r^2=0.44) c) silica (summer-spring p=0.0007, r^2=0.39, winter-autumn p=0.53, r^2=0.02) d) chloride (summer-spring p=0.00003, r^2=0.47, winter-autumn p=0.00002, r^2=0.51). Source: (Struyf *et al.*, 2004); see also Chapter 4

Oxygen depletion during summer in the Seine could be attributed to the high demand by nitrification (Garnier *et al.*, 2006). Although this created favorable conditions for water-

column denitrification, chemical or isotopic techniques could not provide evidence for this process in the TFW zone (Sebilo *et al.*, 2006). In the brackish zone, however, a significant departure of the nitrate isotopic composition from what would be expected from simple mixing of freshwater and marine nitrates suggested coupled nitrification and denitrification. The nitrification distribution in the Seine River was in accordance with results from the Elbe River (nitrifier cell count values, which dropped drastically with increasing salinity (Stehr *et al.*, 1995)), and with modelled patterns in the Scheldt River (Soetaert & Herman, 1995b).

Nitrification is not the first cause of oxygen depletion in every estuary. Within the turbidity maximum of the Seine, a lowered biodegradable fraction of particulate organic carbon indicated that freshwater turbidity maxima are sites of preferential degradation, with a bacterial growth of attached bacteria being on average threefold that of free living bacteria (Servais & Garnier, 2006). Extremely high amounts of CO_2 can be emitted from estuaries, with the Scheldt estuary as record holder (Frankignoulle *et al.*, 1998). Within estuaries emissions were maximal in the freshwater part, *e.g.* in the Scheldt partial pressures of 13,000 µatm were not unusual (Hellings *et al.*, 2001). In the Elbe autotrophy prevailed in most of the estuary, except in the freshwater zone, where an average pCO_2 of 1100 µatm was measured (Brasse *et al.*, 2002).

This enhanced mineralization can affect the distribution of nutrient forms. In the Elbe the turbidity maximum showed a clear decrease of particulate organic P (POP) to 20% of total P, which was otherwise the dominant P species at the seaward side of the estuary (51%). Upstream of the turbidity zone the POP fraction increased to 33% (Van Beusekom & Brockman, 1998). Fe-bound P, the dominant inorganic form, increased from 27% of total P at the seaward side to 57% just upstream of the turbidity maximum, and slightly decreased further upstream to 48%. A similar pattern was found for the Scheldt (Zwolsman, 1994), although only the downstream limit of the TFW zone was included in this study, as zones of maximal turbidity or retention studies of whole estuaries received much more attention with respect to P cycling than the TFW itself. It deserves more attention though. In the Scheldt estuary, 53% of dissolved inorganic P (DIP) (14600 kM), 27% of POP (3600 kM) and 25% of total P (18400 kM) of the estuarine input at the river boundary was retained within the TFW zone (Van der Zee *et al.*, 2007). This retention is important, the more so if it is considered that the water quality improvement that is observed in several estuaries, can cause the nutrient limitation in the coastal zone and in estuaries to shift from N to P (Billen & Garnier, 1997; Billen *et al.*, 2005).

In low turbidity microtidal freshwater systems, the fate of nutrients can be different. At the interface between the watershed and the shallow Rhode River estuary, a small oligohaline to mesohaline sub-estuary of Chesapeake Bay, DIP production was the most pronounced feature, fed by enhanced mineralization of settled POP and dissolution of Fe-oxyhydroxides from sediments and wetlands, especially in summer (Jordan *et al.*, 1991). The freshwater zone was thus not retaining P, but merely transforming it from particulate to dissolved forms. Another important feature was the strong uptake of nitrate by enhanced phytoplankton growth. As a result, the N:P ratio was seasonally changed to low values, contrasting sharply with the adjacent Chesapeake Bay. This also illustrates that not only changes in the pelagic compartment determine the fate of nutrients but that the interaction with sediments and marshes have to be considered as well.

2.2.4.3 Interaction with sediment and wetland vegetation

A key difference between estuaries and non-tidal rivers is the presence of intertidal habitats, such as mudflats, sand bars, and tidal wetlands. Their interaction with the water column received much attention in estuaries, although the TFW are represented relatively little in these studies. Nevertheless, in TFW, intertidal areas and especially North American wetlands have probably been studied more than the pelagic processes.

Freshwater mudflats are known to be (potential) hotspots of denitrification (Seitzinger, 1988). In the Scheldt estuary, denitrification, nitrification, and ammonification differed by almost an order of magnitude between a freshwater station and intermediate brackish stations (Middelburg *et al.*, 1995). The abundant amounts of available nutrients, the flooding regime, oxygen gradients, and factors enhancing sediment-water column exchange such as bioturbation by benthic invertebrates (*e.g.* Pelegri & Blackburn, 1995) are all factors that favor denitrification in sediments.

A negative relation between salinity and denitrification rates has repeatedly been reported (*e.g.* Seitzinger, 1988). Salinity intrusion can have profound effects on the anaerobic microbial and geochemical dynamics of tidal freshwater sediments. In a flow-through experiment, increased nutrient release (ammonium, silicate, phosphate), decreased methanogenesis and a rapid shift to sulfate reduction, with a coincident increase overall organic matter mineralization, accompanied salinity intrusion into previously freshwater riverine sediments (Weston *et al.*, 2006). The role of oxygen variation in DIP release from

sediments is thus probably larger in TFW than in marine bottom layers, because salinity is already a constant factor of enhanced release in marine zones (Jordan *et al.*, 1991).

Rooted macrophytes link sediment biogeochemistry with the biogeochemistry of the overlying water. As a result, the TFW vegetation can have an important impact on nutrient cycling in estuaries. The ecology of European TFW has, with respect to nutrient cycling and exchange, received little attention in the European scientific community, as compared to the scientific research conducted in North America (*e.g.* Bowden, 1984; 1986; 1987; Chambers & Odum, 1990; Khan & Brush, 1994). The few exchange studies focused upon TFW (*e.g.* Simpson *et al.*, 1983b; Childers & Day, 1988; Bowden *et al.*, 1991) were also mainly American. However, recently, the silica and nitrogen cycling in a Scheldt freshwater marsh have been studied in detail, clearly indicating the buffering role the TFW habitats play in nutrient cycling. This study was triggered by a marsh exchange study, which pointed out that N retention and export of dissolved Si (DSi) were equally important dominant features (Van Damme *et al.*, 2009). A summary of these recent advances in research on N and Si-cycling is provided.

2.2.4.4 Silica cycling

TFW contain huge stocks of biogenic Si (BSi), both in sediment and vegetation (Struyf *et al.*, 2005b). Although the total biomass in a reed-dominated TFW is only a fraction of the biomass of a tropical rainforest, the stock of reactive biogenic Si in soil and vegetation is similar (+/- 120 g BSi m^{-2} in vegetation, and 1500 g m^{-2} in the upper 30 cm of soil) (for figures on tropical rainforests: Lucas *et al.*, 1993, Alexandre *et al.*, 1997). Almost all vegetation BSi is in the *Phragmites australis* (hereafter referred to as *Phragmites*) vegetation, where dead shoots can contain up to 8% of BSi relative to dry weight. BSi content in most other species (*Impatiens glandulifera, Salix* spp., *Epilobium hirsutum*) is negligible, while *Urtica dioica* contains relatively high BSi (up to 1% of biomass), but its biomass is not high enough to significantly contribute to the total amount of plant BSi (Struyf *et al.*, 2005b). In a TFW that covered 3500 m^{-2}, 96% of plant BSi was stored in *Phragmites*, while in the total biomass, contribution of reed was only 50%.

BSi is easily soluble if compared to mineral Si, which is considered nearly inert at biological timescales (Van Cappellen, 2003). The high loading of TFW, dominated by *Phragmites*, with such a reactive silica stock, effectively makes them dissolved silica buffers in the estuarine environment. Dissolution of BSi enriches the porewater with dissolved silica compared to the

estuarine pelagic water. Porewater DSi concentrations in the TFW along the Scheldt can be one order of magnitude higher than the concentration of DSi in tidal inundation water in summer. Averaged yearly, the porewater DSi concentrations are about 500 µM (or 14 mg L^{-1}), while DSi concentrations are maximally around 300 µM in the pelagic, and can drop as low as 10 µM in summer there (Struyf *et al.*, 2005a, b).

At high tides, when the wetland is flooded, the porewater is entrained by inundation water with a lower DSi concentration. This mixing of DSi-enriched porewater with DSi-poor flooding water results in a steady outflow of DSi from the wetland towards the main estuarine river. This outflow is mainly focused in the seepage water, which is the water flowing out of the wetland between two bulk-tides, the period of ca. 3 hours during which the wetland is flooded with large volumes of water (Barendregt *et al.*, 2006). The seepage water has been in close contact with wetland sediments and litter. As a result of this BSi-recycling mechanism, TFW act as buffers within the estuarine Si-cycling: they will export most DSi, when the DSi-content in the inundation water and the pelagic is mostly depleted (Struyf *et al.*, 2006). DSi ratio to N and P is extremely important in the occurrence of harmful phytoplankton blooms in the coastal region. As DSi-buffers, tidal wetlands probably partly buffer human over-input of N and P into estuaries. Both sediment and vegetation play a similar role in this mechanism, that of a recyclable stock of Si. However, the rate of BSi dissolution and the amount of BSi stored in both stocks differs.

Phragmites is a relatively small but rapidly recycled sink for Si. Once reed shoots collapse, the BSi in the shoots dissolves very rapidly. Based on decomposition experiments, carried out in both winter and summer at different flooding frequencies (Struyf *et al.*, 2007), after one year all BSi has leached from the decomposing shoots. Taking into consideration the highly dynamic character of the reed vegetation, we can effectively conclude that the *Phragmites* community is almost self-sufficient in regard to Si-use, with almost 100% recycling of biologically fixed Si in a single year. Similar high recycling efficiencies were observed in temperate and tropical forests (Bartoli, 1983; Conley, 2002). Average DSi-release from the *Phragmites* litter layer was approximately 0.07 kg m^{-2} y^{-1}. Sediment on the other hand was by far the largest sink for BSi in freshwater wetlands, mainly from import with deposited sediments (Struyf *et al.*, 2007). BSi dissolves much more slowly than plant BSi: although the source for potential BSi dissolution is more than ten times the potential source for plant BSi dissolution, only about 0.04 kg Dsi m^{-2} y^{-1} is released from the sediment. The complete yearly

flux schedule of Si between the different compartments in a TFW marsh along the Scheldt is shown in Fig. 2.5.

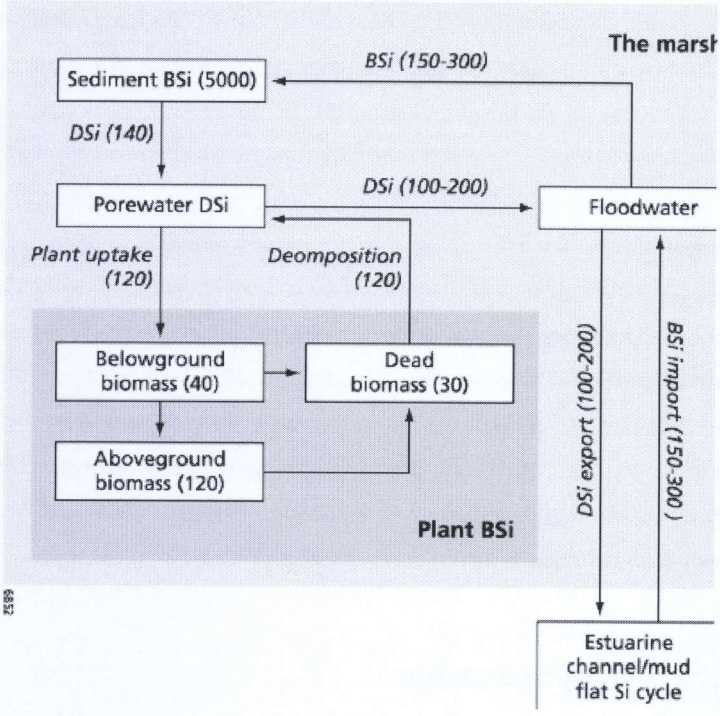


Fig. 2.5: The freshwater wetland Si cycling in a 3500 m^2 marsh along the Scheldt. All numbers are in kg Si. Fluxes (in italics) are indicated as yearly total fluxes. Stocks of Si in sediment (upper 30 cm) and vegetation are indicated in bold, and are the total stocks for the complete 3500 m^2 area. Stocks in vegetation are for the peak of the growing season. Stocks in sediment are not subject to seasonal change. The marsh and the estuarine channel are indicated as interacting compartments.

2.2.4.5 Nitrogen cycling

Wetlands are known to play an important role in the retention of nitrogen along the aquatic continuum, and TFW marshes are no exception. Providing a large surface of sediments and biota to interact with the inundating water, wetlands have the potential to promote processes that change nitrogen speciation, and that increase the potential for retention in vegetation or sediment (Gribsholt *et al.*, 2005; 2006). However, until recently, surprisingly little data supported this hypothesis for TFW marshes.

Recent whole ecosystem N^{15} labeling experiments in a small TFW along the Scheldt have provided experimental evidence for the large potential of the freshwater intertidal to enhance

nitrogen retention and processing (Gribsholt *et al.*, 2005; 2006). The wetlands strongly stimulate the nitrification of ammonia to nitrate, and transformation of nitrogen speciation (through both denitrification and nitrification) was equally important as the (partly temporal) retention of N. Roots, aboveground vegetation, sediment, and plant litter retained about 4% of the added ammonia, while 9% of the added ammonia was nitrified. Although denitrification was not directly measured during the experiment, up to 14% of the added ammonia was estimated to be removed ultimately from the estuarine ecosystem through denitrification in the TFW.

The results suggested that annually about 3% of the yearly ammonium load to the Scheldt is nitrified in TFW. Although the total transformation and retention of N in the freshwater intertidal area is for the moment still very small compared to pelagic processes, future plans to increase the total area of TFW along the Scheldt fourfold (Flemish decree VR/PV/2005/9-point 22 and VR/PV/2005/29-point 114) might alter this. Indeed, for the near future restoration plans along the Scheldt are planned to increase safety against extreme flooding events and to allow the establishment of an estuarine ecosystem. TFW and sediments thus show strong potential benefits.

2.3 Aquatic primary production

Primary production is defined as the rate at which inorganic carbon is incorporated in the food chain through photosynthesis. Gross primary production (GPP) is the rate of photosynthetic energy conversion of light into chemical energy; net primary production (NPP) is gross production minus respiration (Platt *et al.*, 1984). A review on estuarine primary production is given in Heip *et al.* (1995). Here, an update of knowledge on the aquatic primary production in TFW is presented.

Three important compartments may be distinguished: phytoplankton, micro-phytobenthos, and macrophytes. The relative contribution of each of them probably depends mainly on the surface-volume distribution of the system, the tidal amplitude, and the turbidity. Submerged macrophytes preferentially occur in low-hydrologic-energy systems with good light conditions (*e.g.* Capers, 2003). For instance, in the tidal Hudson River, submerged vegetation production was in the same range as phytoplankton production, but due to the scarce distribution of shoal habitat, the area-specific contribution to the system carbon balance was

marginal (Howarth *et al.*, 1996). In systems with higher hydrologic energy, macrophytes are confined to the tidal marshes.

Biomass and production data for micro-phytobenthos in TFW are extremely scarce, in part because extracting them from the sediment is difficult. Nevertheless, a comparison between freshwater and brackish tidal mudflats showed clear differences. Epipelon (defined as organisms moving freely in and on the sediment) and epipsammon (defined as organisms that live in close association with individual sand grains) were the dominant organisms at the brackish sites (Muylaert *et al.*, 2002). In TFW mudflats these groups were nearly absent; instead, the sediments were dominated by pelagic diatoms that settled onto the substrate. This was ascribed to the dynamic character of TFW mudflats. As the level of tidal wetlands increases following an increasing tidal range (Temmerman *et al.*, 2003), while the system remains confined between dikes, the slopes of intertidal mudflats logically must increase. It is hypothesized that this effect is largest in the TFW where the estuary is narrowest, and that micro-phytobenthos is related with mudflat slope. This chapter is further restricted to phytoplankton.

2.3.1 General pattern of pelagic primary production

Information on pelagic primary production in TFW is scarce. In recent years, TFW habitats in the Scheldt estuary have been targeted in several studies. Before studies of pelagic primary production in TFW were undertaken, it was generally believed that primary production of phytoplankton increased towards the mouth of an estuary, where a decrease of nutrient concentrations would be more than compensated for by the increased water transparency (Heip *et al.*, 1995). This picture has changed during the last few years. In the tidal freshwater zone of the Scheldt, NPP can vary from negative (Soetaert & Herman, 1995a) to high positive values (Kromkamp *et al.*, 1995; Mulaert *et al.*, 2005). In the Scheldt, the tidal freshwater zone showed higher values of chlorophyll *a* than the brackish part (Fig. 2.6; Muylaert *et al.*, 2000; Van Damme *et al.*, 2005) and high phytoplankton production values were measured in several studies (Table 2.1). Along the salinity gradient of both the Scheldt and Elbe estuaries, total cell abundance and biomass were highest at the oligohaline stations (Muylaert & Sabbe, 1999). In the Gironde estuary cell numbers and biomass values were an order of magnitude lower but followed the same pattern (Muylaert & Sabbe, 1999). Maximum values of production, biomass or chlorophyll *a* occurred in the TFW zone in the Seine, although measurements were restricted at low discharge regimes (Garnier *et al.*, 2001), in the Weser

(Schuchardt & Schirmer, 1991) and the James River estuary (Moon & Dunstan, 1989). The pattern that has emerged from these studies is that TFW are in general more productive than their brackish or saline counterparts, although a possible dilution effect is not always considered. This decline has been ascribed to osmotic stress at the freshwater-saltwater interface, *e.g.* in the Elbe (Kies, 1997). A specific experiment in the Scheldt estuary, however, showed that, although freshwater and brackish water phytoplankton was negatively affected by, respectively, an increase or decrease in salinity, this effect was not strong enough to explain the phytoplankton distribution along the salinity gradient (Lionard *et al.*, 2005). Neither could suspended matter concentrations explain the difference, as values were similar in the turbidity maximum of the freshwater-saltwater interface and the freshwater zone. In many estuaries, however, the freshwater zone is more shallow than the brackish part, *e.g.* in the Scheldt (Muylaert *et al.*, 2005) and the Elbe (Rolinski, 1999). In those cases a change of the euphotic depth:mixing depth ratio could explain the distribution along the salinity gradient, although the Elbe is less well mixed than the Scheldt. In many cases, the high production rates in the TFW zone were attributed to low freshwater discharge and hence longer residence times (*e.g.* Moon & Dunstan, 1990; Schuchardt & Schirmer, 1991; Muylaert & Sabbe, 1999; Muylaert *et al.*, 2005), thereby often pointing to the fact that blooms occurred during summer or autumn periods, when precipitation was low. On the contrary, when river discharges into the TFW zone were high, low production values were measured in the York River (Sin *et al.*, 1999) and Elbe (Muylaert & Sabbe, 1999) estuaries.

In the Scheldt estuary, clear differences in phytoplankton species composition were observed between the tributary (non tidal) rivers and the TFW zone (Muylaert *et al.*, 1997; Muylaert *et al.*, 2000). Diatoms were found to be the dominant phytoplankton group in the TFW reaches, while chlorophytes dominated the tributary rivers, especially in summer. Changes in phytoplankton community composition along the riverine-estuarine transition were ascribed to different adaptations of the phytoplankton community to the light environment. The general idea was that diatoms are adapted to low light levels and are therefore capable of surviving in the turbid estuary, while green algae depend on relatively high light intensities and would therefore be expected to survive only in the river (Richardson *et al.*, 1983).

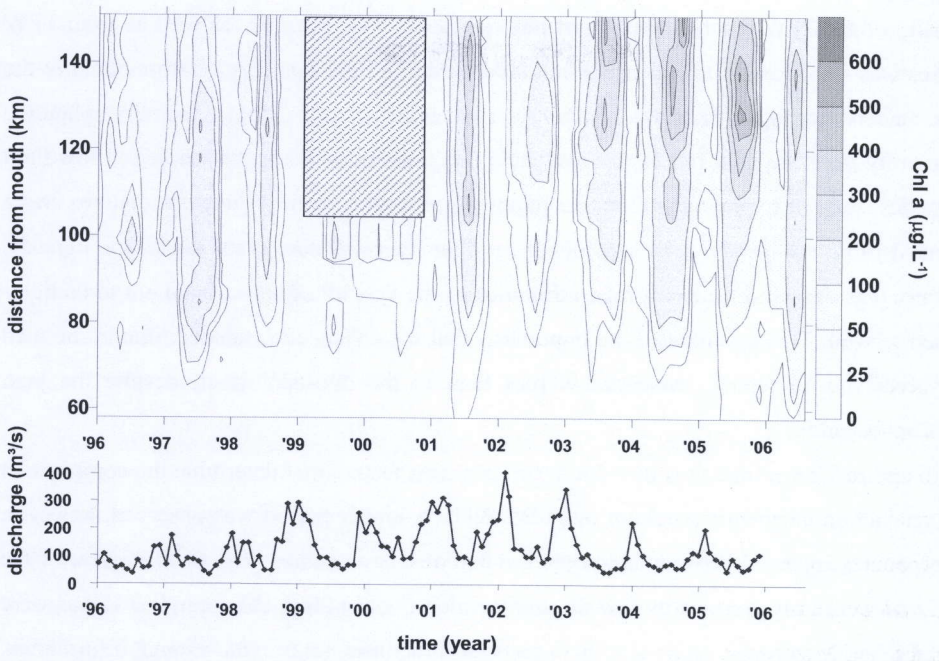


Fig. 2.6: Chlorophyll *a* (Chl *a*) concentrations in the Belgian part of the Scheldt estuary and river discharge (Schelle, source Flemish Administration of Waterways and Sea); update after Van Damme *et al.* (2005); see also Chapter 3

Table 2.1: Phytoplankton production, total cell count, and chlorophyll *a* (Chl *a*) values in tidal freshwater areas; GPP=gross primary production; NPP= net primary production; Chl *a* is expressed as yearly maxima (<) or yearly average values (interval).

		GPP	NPP		Total cell counts	Chl a
		g C $m^{-2} y^{-1}$	g C $m^{-2} y^{-1}$	g C $m^{-3} d^{-1}$	cells ml^{-1}	mg L^{-1}
Hudson River	Cole et al. (1992)	130-380	70-204			20-40
	Howarth et al. (1996)	130-380	20			20-40
York River estuary	Sin et al. (1999)	< 30				< 10
Chesapeake Bay	Moon & Dunstan (1990)					< 115
Scheldt	Van Spaendonk et al. (1993)	900				< 270
	Kromkamp & Peene (1995)		388			< 75
	Kromkamp & Peene (2005)		500			28-43
	Soetaert et al. (1995)			-20 - +10		< 50
	Muylaert & Sabbe (1999)				10000-22000	
	Muylaert et al. (2005)		108-294			< 111
Elbe	Muylaert & Sabbe (1999)				100-36000	
	Schuchardt & Schirmer (1991)					50-70
Weser	Schuchardt & Schirmer (1991)					50
Gironde	Muylaert & Sabbe (1999)				800-1100	
Seine	Garnier et al. (2001)			500-1000		

However, when incubated at a light intensity corresponding to the mean underwater light intensity of the TFW reaches, growth of phytoplankton from the river as well as from TFW reaches was significantly lower than when incubated at a light intensity corresponding to the mean underwater light intensity of the river (Lionard *et al.*, 2005). The phytoplankton community from the tidal freshwater reaches did not appear to be better adapted to low light intensities than the phytoplankton community from the river. Although diatoms were expected to be less sensitive to a reduction in light intensity than green algae, the opposite response was observed. The non-tidal tributaries of the Scheldt estuary turned out to be light-limited as well. This accentuated the hypothesis that the enhanced residence time in the tidal part gives rise to higher production values than in the non-tidal river, despite the high estuarine turbidity.

Depth and residence time thus turn out to be dominant factors that determine the composition and production of pelagic plankton in TFW. When a longer period was observed, however, discrepancies appeared between chlorophyll *a* and discharge values (Fig. 6). Both years 1996 and 2004 were characterized by low discharge values, yet in 2004 chlorophyll *a* values were much higher. Monitoring on a monthly basis does sometimes not provide enough information. In 1996, a specific short-term high-frequency monitoring effort revealed that during a storm at the end of August a peak discharge occurred from 10 to 280 $m^3 s^{-1}$. As a result of this event, diatom biomass dropped from 3.5 to 1.0 mg C L^{-1}, while *Scenedesmus* and coccal green algae in general did not decrease, NPP decreased to roughly 20% of its initial value, and DSi concentrations increased (Muylaert *et al.*, 2001). This drop lasted, in combination with a drop in temperature and irradiance, for the rest of the season. In 1998 another peak discharge event was followed (from 50 to 250 $m^3 s^{-1}$), this time in spring, but this time the effects were less pronounced (Muylaert & Vyverman, 2006).

Because of these clear indications that standing stock, production, and community composition can vary considerably within the TFW, it is surprising that the TFW zone is often considered as a single entity. In many estuarine studies the tidal freshwater zone is not considered over its full length and is considered to only be a boundary of the estuary (*e.g.* Van Spaendonk *et al.*, 1993; Kromkamp *et al.*, 1995; Kromkamp & Peene, 2005; Soetaert & Herman, 1995a; Goosen *et al.*, 1999). When variation was measured within the TFW zone, longitudinal patterns other than increasing upstream trends were found. Within the long TFW zone in the Hudson River, for example, production was higher in the mid-section compared to

the upper limit of tide (Cole *et al.*, 1992). A closer look at the phytoplankton community is therefore an essential step in understanding production variation within the TFW.

2.3.2 Tidal freshwater communities

In the Scheldt estuary, the TFW was characterized by two separate plankton communities (Fig. 2.7) and the distribution of these communities along the longitudinal estuarine axis corresponded with the energy distribution pattern. The TFW has a critical point, upstream of which the discharge energy exceeds the tidal energy and the freshwater velocity becomes larger than the tidal velocity (Chen *et al.*, 2005). Upstream of this critical point the river discharge has a considerable influence on tidal damping, primarily through friction (Horrevoets *et al.*, 2004). This cross point is situated where the cross-sectional area of the estuary approaches the cross-sectional area of the non-tidal upstream boundary. It can rightly be regarded as the boundary between the estuarine and the riverine part of the TFW. This is reflected in the plankton community structure: where tidal energy dominates over river discharge, the phytoplankton community was dominated by the taxa *Actinocyclus normanii* (Gregory ex Greville) Hustedt and *Aulacoseira granulata* (Ehrenberg) Simonsen in winter and by *Cyclotella scaldensis* Muylaert & Sabbe in summer (Muylaert *et al.*, 2000). *Actinocyclus normanii* was also the dominating species during the seasonal chlorophyll *a* maximum within the TFW reaches of Weser and Elbe, which occurred in late summer / autumn (Schuchardt & Schirmer, 1991; Rehbehn *et al.*, 1993). Where river discharge dominated tidal energy, *Stephanodiscus hantzii* Grunow and *Scenedesmus* spp. represented the community, but their densities declined as the tidal energy increased. *Stephanodiscus hantzii* also dominated the limnetic part of the Elbe estuary (Muylaert & Sabbe, 1999).

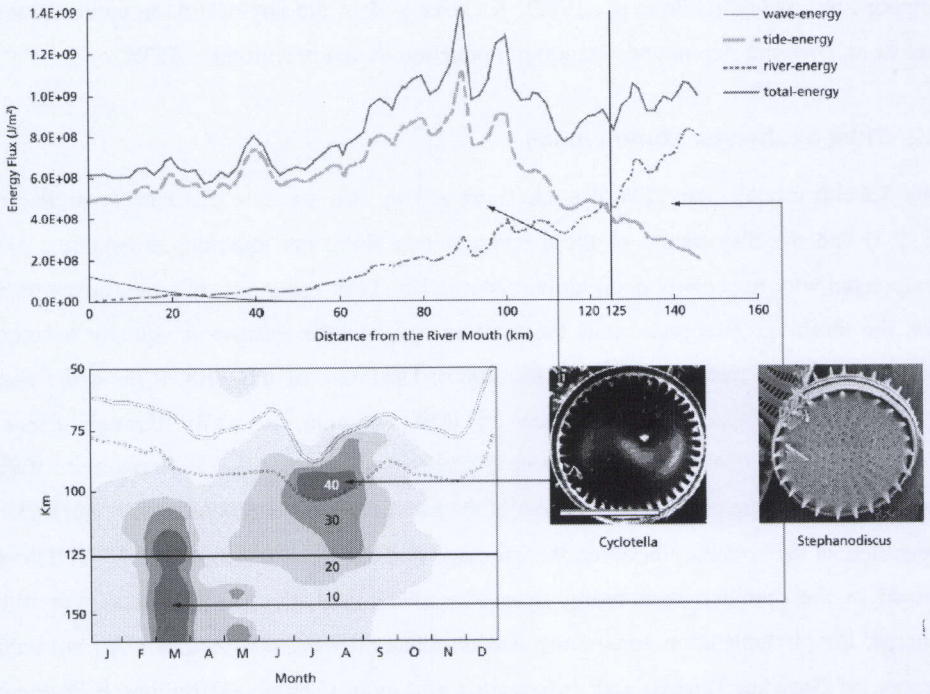


Fig. 2.7: Combining the spatial chlorophyll *a* concentration distribution (below) (Source: Muylaert *et al.*, 2000) and energy distribution in the Scheldt estuary (top) (Source: Chen *et al.*, 2005), with electron microscope images (Source: K. Muylaert pers. comm.) of the dominating species in each bloom. Spring and summer bloom occurred under different energy conditions.

Thus, it is likely that in various estuaries the transition point between discharge and tide-dominated hydrology is reflected by a succession between a phytoplankton community of riverine origin to one that is autochthonous to the estuary. Riverine communities of course have their own variability, which can affect input in estuaries, as was demonstrated, *e.g.* in the Seine, where a seasonal succession of diatoms and Chlorophyceae caused silica depletion in summer (Garnier *et al.*, 1995).

Another reflection is that determining the actual phytoplankton species composition is one thing, determining what assemblage corresponds with a good condition is yet something else. In Chesapeake Bay, paleontological indicators in dated sediment cores were used for the purpose of reconstructing a long-term environmental history of the bay. Analysis of the data indicates that sedimentation rates, anoxic conditions, and eutrophication have increased in the Chesapeake Bay since the time of European settlement (Cooper & Brush, 1993). For example, since initial land clearance around 1760, sedimentation rates have increased from as low as

0.02 cm y^{-1} to an average 0.22 cm y^{-1}, indicating an increased risk of light limitation. Diatom community structure showed a steady decrease in overall diversity since 1760 and the centric:pennate ratio increased significantly since 1940. While this approach to characterization of the plankton community provides interesting information, care should be taken, as sea-level changes and estuarine morphological evolution most likely caused shifts in the location of the TFW zones.

A comparison of measured production between freshwater tidal communities is unavailable, although a different response on light conditions and nutrients is expected or demonstrated (*e.g.* Lionard *et al.*, 2005). TFW have specific phytoplankton assemblages. Whether this is incorporated sufficiently in existing ecological models that are used to reconstruct or predict primary production is a relevant question. In many estuaries, an investigation into communities in the freshwater zone is still needed, as the TFW zone of estuaries is in most cases treated as one entity. This lack of basic knowledge is striking, when one realizes that primary production is the basis of the estuarine food chain, and that a shift in balance from autotrophy to heterotrophy can have a significant impact on oxygen concentration and thus on the faunal diversity. Refining the knowledge on primary production is therefore a need that is expressed not only by biologists but also by modellers.

2.3.3 Complications in measuring and modelling

GPP is commonly expressed in terms of specific productivity, *i.e.*, per unit mass of chlorophyll *a*. Chlorophyll *a* is thus used as a proxy for photosynthetically active biomass. In this way, GPP is only a potential value of specific photosynthetic activity (*i.e.* the carbon incorporation rate per unit mass of phytoplankton at well-defined values of light intensity, temperature, and nutrient content). However, in natural systems, these parameters usually vary both in space (for example, light intensity decreases with water depth) and time (*e.g.* according to discharge). To estimate the actual carbon fluxes due to photosynthesis during a given period, gross primary productivity has to be multiplied by the phytoplankton mass and must then be integrated over space and time, leading to the value of GPP. When respiration is determined in an analogue way and subtracted from GPP, NPP is determined as presented in Table 1. Many different methods are used to determine GPP and NPP, making it difficult to develop precise values of GPP or NPP. Some occurring problems are listed in the following sections.

2.3.3.1 Light intensity

GPP is often determined by measuring C^{14} isotope incorporation through incubations. Incubations for measuring GPP have the disadvantage of being static, so that the light intensity is usually not simulated according to the short-term variation of the natural conditions. Model results based on short-term variability data showed that the description of phytoplankton growth must operate at a time resolution sufficiently high to describe the interference between solar and tidal driven physical forcing functions (Desmit *et al.*, 2005). It was shown that in shallow to moderately deep systems, simulations using averaged, instead of time-varying forcing functions, lead to significant errors in the estimation of phytoplankton productivity. The highest errors were observed when the temporal pattern of light penetration, linked to the tidal cycle of solids settling and resuspension, were neglected.

In order to overcome the disadvantage of static incubations, a so-called 'turbulence incubator' was designed (Gocke & Lenz, 2004). The incubator allowed simulating the changing light conditions for vertically mixed phytoplankton cells by moving sample bottles in a controlled way. With this method, significantly higher primary production rates were obtained than in static incubations *ceteris paribus*. Short-term variation was not taken into account in any of the GPP or NPP values in Table 1.

2.3.3.2 Nutrients

If one would implement reference conditions for phytoplankton in Chesapeake Bay, this would require an increase in light transparency of the water column and lower concentrations of dissolved inorganic nitrogen and orthophosphate (Buchanan *et al.*, 2005). Limitation can shift from one element to another if conditions change (*e.g.* Billen *et al.*, 2005). But the fate of lesser limiting nutrients is every bit as important as that of the limiting nutrient (Flynn, 2005). Phytoplankton species have multi-nutrient growth dynamics. Therefore, neglecting a nutrient in monitoring or modelling can have consequences on the modelled primary production results. Soetaert & Herman (1995a, b) obtained the results by a model that took into account N, but not P. As the limitation sequence between these two elements changed in the Scheldt (Billen *et al.*, 2005), this model certainly needs improvement on this point.

Limitation of diatom growth by DSi is a major issue in coastal zones and the marine zone of estuaries, where shifts in community structure have been related to it (*e.g.* Cugier *et al.*, 2005). But also in the TFW, DSi can show depletion (Van Damme *et al.*, 2005), even beyond diatom growth limitation (T. Maris pers. comm.). These shortages occurred during summer

months, concurrently with peaking rates of NPP (between 500 and 1500 g C m^{-2} y^{-1}) (T. Cox pers. comm.). However, the silica processing by the tidal freshwater community probably needs different modeling formulations than the marine zone.

2.3.3.3 Biomass specific rates

Due to different estimates of respiration rates, a discrepancy in NPP values between different authors was reported for the Hudson River (Table 1). A common failing is measurement of biomass by chlorophyll (Flynn, 2005). The relationship between chlorophyll *a* and biomass is not constant but may vary over 5- to 10-fold with growth irradiance and nutritional status. The chlorophyll *a*:biomass (chlorophyll *a*:C) ratio is important for determining GPP as well as respiration. With the very specific and variable light conditions and nutrient status in TFW, it is essential to determine local chlorophyll *a*:C ratios. Preliminary results revealed that in the TFW of the Scheldt this ratio ranged between 1 and 70, with a mean of 15 (M. Lionard pers. comm.). These values are exceptionally low. If they can be confirmed, this would imply that modelling of phytoplankton production in TFW needs a full revision.

2.4 Conclusions

This study presented a state-of-the-art synthesis concerning aquatic primary production and its determining factors in the TFW zone of estuaries. Although there was much less information available compared to their more saline counterparts, enough arguments were assembled to illustrate the importance, complexity, variability, and uniqueness of the TFW. All factors that could be related to primary production can strongly interact. There are TFW of all kinds, high or low hydrologic energyc, dominated by tide or discharge, turbid or clear. This diversity is reflected in the community composition of the primary producers, but their adaptive behavior is sometimes contrasting with general ideas.

This synthesis provides a basis for deeper comparative estuarine research that could lead to quantified relations between determining factors. However, the scarceness of data, together with weaknesses in methodology for measuring or modelling primary production, is so striking that it can be postulated that the time is not yet ripe for providing an accurate and detailed picture of primary production in TFW. Nevertheless, the time is ripe for starting to work on it, as it is clear what must be done to fill in the gaps. The basis of the food web, in zones through which the entire discharge of whole catchments passes, offers enough potential

to deserve sound scientific attention. Restoration and management can after all only be successful if at least the actual status is known.

Acknowledgements

The authors wish to thank the Flemish Administration for Waterways and Maritime Affairs, division Zeeschelde, and the Fund for Scientific Research for supporting TFW research in the Scheldt estuary.

Chapter 3

Spatial and temporal patterns of water quality along the estuarine salinity gradient of the Scheldt estuary (Belgium and The Netherlands): results of an integrated monitoring approach

Van Damme S., Struyf E., Maris T. Ysebaert T., Dehairs F., Tackx M., Heip C., & Meire P.

Hydrobiologia 540: 29-45 (2005)

Abstract

This chapter presents the results of seven years of integrated monitoring along the Scheldt estuary. The combination of two datasets resulted in a full description of the estuaries water quality parameters from the mouth to the upper boundary, including an extended fresh water tidal part. A synthesis of the monitoring results and all relevant ecological knowledge on the Scheldt allowed to identify opportunities to optimize its management. The results show that the effect of discharge on salinity has a distinct maximum in the polyhaline to mesohaline transition area. Oxygen conditions, nitrogen removal and phytoplankton regulation can be enhanced and improved through management measures within the estuary. To lower carbon and phosphorous loads however measures should be taken within the catchment. To restore most of its ecological functions the estuary needs more space. Optimal locations to address specific functions can be derived from the monitoring results.

3.1 Introduction

Estuaries are cited among the most productive biomes of the world (Costanza *et al.*, 1993). They support important biogeochemical processes that are central to the planet's functioning, *e.g.* nutrient cycling (Billen *et al.*, 1991; Costanza *et al.*, 1997). Estuaries are the interface between terrestrial and coastal waters. They often are characterized by steep chemical gradients and complex dynamics, and these can result in major transformations in the amount, chemical nature and timing of the flux of material along these river-sea transition zones. As estuaries concentrate waters from very large land surfaces into relatively small water bodies (Heip *et al.*, 1995), the biogeochemical processes and trophic interactions within estuaries can play an important role in the management of water quality problems. This ecological functioning is considered to be of major concern, as estuaries offer the last opportunity to manage water quality problems before they become uncontrollable in the coastal waters.
However, this huge potential of ecological functions is far often repressed by human impact (Suchanek, 1994; Gray, 1997). The Scheldt estuary is not an exception. It is characterised by a notorious history of pollution and eutrophication (Wollast, 1988; Boderie *et al.*, 1993), and the estuarine intertidal habitats have suffered from important area reduction and quality degradation (Meire *et al.*, this volume). The Schelde estuary nevertheless has some high ecological values, being internationally important for several bird species (Van den Bergh *et al.*, this volume), and with large parts of the estuary being designated under the Ramsar Convention and European Birds and Habitat Directive. Although the risk of a further deterioration and habitat loss is still present, there is a growing awareness that conservation and restoration of the estuarine ecological functions is needed. In the past only some local measures have been undertaken, but it is only recently recognized that a restoration of ecological estuarine functioning requires an integrated, whole system approach. One of the fundamental steps in establishing such an integrated water management approach, is the development of an integrated monitoring programme. For the Scheldt estuary, ecological data in general and water quality monitoring data in particular are amply available, but they are scattered over many sources and ecological research focussed until recently mainly on the marine and brackish part of the estuary (Van Damme *et al.*, 1995). The freshwater part received less attention (*e.g.* De Pauw, 1975; Hummel *et al.*, 1988), although it covers more than one third of the total length of the estuary. A serious attempt to integrate ecological estuarine research at the scale of the whole Scheldt estuary, including the freshwater part, was initiated through the OMES program (Meire *et al.*, this volume). This program was set up to

fill in knowledge gaps in order to allow fundamental ecological management of the whole estuarine system through the development of an ecosystem model. Within the frame of this research program a long-term water quality monitoring program was set up in 1995 to monitor all essential parameters from the mouth till the upper boundary, including the freshwater part. The monitoring program included sufficient spatial sampling to allow assessments of variability at the scale of the ecosystem. To achieve this programme, an ongoing monitoring program from the Netherlands Institute for Ecology – Centre for Marine and Estuarine Research (CEME), covering the marine and brackish zone of the estuary (*e.g.* Kromkamp *et al.*, 1995), was extended with an OMES monitoring program covering the Belgian part of the estuary. The combination of these data allowed for the first time the presentation of an actualised full description of the basic water quality of the whole Scheldt estuary. In this study, spatial and temporal variability in suspended particles, nutrients and chlorophyll *a* concentrations is described for the period 1995-2002. The major underlying processes and mechanism are discussed and some opportunities to optimise ecological water management are proposed.

3.2 Material and Methods

3.2.1 Study area

The Scheldt estuary is located in Northern Belgium (Flanders) and the Southwest Netherlands (Fig.1). It extends from the mouth at Vlissingen (km 0) till Gent (km 158); there tidal movement is stopped through a complex of sluices. The lower and middle estuary, the Westerschelde (55 km long), is a well mixed region characterized by a complex morphology with flood and ebb channels surrounding several large intertidal mud and sand flats. The surface area of the Westerschelde is 310 km^2, with the intertidal area accounting for 35% of the area. The average channel depth is approximately 15-20 m. Near the Dutch/Belgian border the estuary narrows and becomes characterized by a single tidal channel and is called Sea Scheldt (105 km long). The surface of the Sea Scheldt amounts to only 44 km^2. The Sea Scheldt is further divided into the Lower Sea Scheldt, stretching from the Dutch-Belgian border to Antwerpen, and the Upper Sea Scheldt, stretching from Antwerpen to the upstream boundary at Gent. The major tributaries of the estuary are the Rupel (tidal), the Durme (tidal) and the Dender (non-tidal). The total length of the river, including both estuary and upper river, is 355 km. The catchment area of the Scheldt is 20,331 km^2. In this area about 10.4

million people are living, forming a dense population of on average more than 5 ind./ha. Large efforts for industrial and municipal waste water treatment has been undertaken during the last decade in Flanders, but still untreated municipal waste water is being discharged into the estuary, with the city of Brussels as the most prominent example. The untreated municipal wastewater of Brussels reaches the estuary through the Rupel tributary near Schelle (km 90). Agriculture in the catchment area is intensive, and is responsible for a considerable part of the nutrient inputs to the estuary (Baeyens *et al.*, 1998). Some large industrial areas are concentrated beside the estuary: near Gent, Antwerpen and Vlissingen.

3.2.2 Sampling

During both the CEME and OMES monitoring cruises surface water samples were taken monthly in the middle of the river from a ship. In the period March-May, during spring phytoplankton bloom, one additional CEME cruise was organized per month. The results presented here deal with the period December 1995 – December 2001, as the OMES campaign started in December 1995. The CEME monitoring was divided over two subsequent days: a first cruise running from Vlissingen to Hansweert and a second cruise from Hansweert to Temse. The second CEME campaign cruise matched the first campaign cruise of the OMES program, running from the Dutch/Belgian border to Dendermonde. The next day the stations between Dendermonde and Gent were monitored, so that the estuary was each month fully covered within a time span of three days The CEME campaign covered 17 stations between Vlissingen and Temse; the OMES campaign started at the Dutch-Belgian border, and covered 16 stations along the longitudinal gradient of the Sea Scheldt (Fig. 3.1). In this way the zone between the Dutch-Belgian border and Temse was overlapping in the two campaigns.

The Administration of Waterways and Sea (AWZ) continuously measures discharge of the Bovenschelde (the Schelde just upstream Gent, where tidal influence is stopped by sluices), the Dender and the Rupel, and we calculated daily average discharges using that data set.

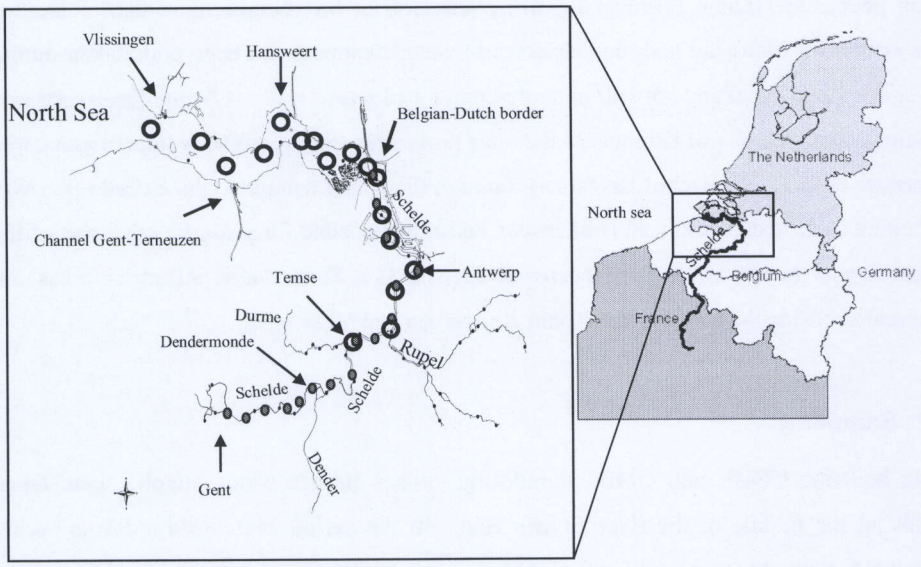


Fig. 3.1: Map of the Scheldt estuary

3.2.3 Analysis

Analytical methods were as much as possible conducted in a similar way for both monitoring programmes, but small differences existed. During the CEME cruises, temperature, oxygen saturation, salinity and pH were measured *in situ* using a Water Quality Multiprobe Hydrolab H20. During the OMES cruises, temperature and oxygen were measured *in situ* with a 'WTW OXI 91' oxygen-meter, salinity was measured with a 'WTW LF 91' conductivity-meter, and pH was measured with a WTW pH 330 pH-meter.

Samples were stored at 4°C and were analyzed within 24h after sampling. CEME partner analysed NO_3^--N, NO_2^--N, NH_4^+-N, orthophosphate (DRP), dissolved silica (DSi) and total phosphorous (totP) (after destruction in H_2SO_4 and $K_2S_2O_8$) colorimetrically using a SKALAR SA 4000 segmented flow analyzer, while SO_4^{2-}-S was analysed using a SKALAR SA 2000. Excepted for DSi, analysed by ICP-OES (Iris®), OMES partners applied the same methods as CEME but using a SKALAR SA 5100 colorimeter instead. Total Dissolved Inorganic Nitrogen (TDIN) is the sum of NO_3^--N, NO_2^-N and NH_4^+-N.

Samples for dissolved organic carbon (DOC) were filtered on Whatman GF/C glassfiber filters of 1.0 µm nominal porosity (CEME), or on Gelman glassfiber filters of 0.45 µm nominal porosity (OMES). For DOC determination, a preliminary treatment with H_2SO_4 acidification and flushing with nitrogen gas to remove background CO_2 concentration was

performed at CEME and in OMES. DOC was then set free by UV-irradiation, and analysis of CH_4 on a SKALAR coupled FID (CEME), or further oxidation to CO_2 and analysis using a SKALAR (phenolphtalein 550 nm detection; OMES).

Suspended matter (SPM) was determined gravimetrically after filtration on pre-combusted Whatman GF/F filters. Particulate organic carbon (POC) was determined on the same filters using a Carlo Erba element analyzer after Cr_2O_3 and $AgCo_3O_4$ catalysed oxidation and segregation on a Haysep-Q-column (CEME & OMES).

Samples for analysis of chlorofyl a (Chl a) were first filtered on pre-combusted Schleicher Schuell nr. 6 filters (CEME) or 45µ Sartorius filters (OMES). Chl a was by extracted in 90% acetone and analysed using reversed phase HPLC (Waters Fluorescence detector 474, excitation at 430 nm, emission at 650nm; CEME); or set free after addition of N,N-dimethylformamide, and analysed colorimetrically at 647 and 664nm (OMES).

Because sometimes a different methodology was used by CEME and OMES, a Wilcoxon Rank-Sum test was performed on results for a common sampling station at Antwerp, to test the significance of the differences between CEME and OMES data (Table 3.1). The comparison showed concordance for most parameters. Only for SPM, total P and pH did the datasets not match. In the present paper we used the OMES data set for SPM, total P and pH for the overlapping zone.

Table 3.1: Results of a Wilcoxon Rank-Sum test to test the significance of the differences between CEME and OMES data of a common sampling station at Antwerp. The p-values of significant differences are in bold. (t° = temperature, O_2 (%) = oxygen saturation, DRP = dissolved reactive phosphate = orthophosphate, tot P = total phosphorous, DSi = dissolved silica, SPM = suspended matter, POC = particulate organic matter, Chl a = chlorofyl a, DOC = dissolved organic carbon)

Parameter	n	Z	p
t°	85	0.32	0.75
pH	81	-4.99	**0.00**
Salinity	83	-0.87	0.39
O_2 (%)	81	0.09	0.93
NO_3^-	85	0.20	0.84
NH_4^+	85	0.43	0.67
NO_2^-	85	-0.59	0.55
DRP	85	0.28	0.78
totP	85	3.10	**0.00**
DSi	79	0.46	0.64
SPM	65	-3.01	**0.00**
POC	65	1.02	0.31
Chl a	65	1.69	0.09
DOC	59	-1.39	0.16

The monitoring results are presented graphically using the surface mapping system software 'SURFER', version 5.01. Interpolation was performed using linear ordinary kriging, radius anisotropy 1/100. Statistics were performed using S-Plus 2000. The data for sampling points common to CEME and OMES cruises were aggregated and averaged per station before they were included in the dataset.

3.3 Results

3.3.1 Hydrology

The average yearly discharge at Schelle (km 103) varied from a minimum of 78 $m^3.s^{-1}$ in 1996 to a maximum of 191 $m^3.s^{-1}$ in 2001 (Fig. 3.2). Over this period the discharge increased year by year; in 2002 a similar discharge was observed as in 2001. There was a clear seasonal variation with maxima in winter and minima in summer (Struyf *et al.*, 2004). Average monthly discharge was strongly related to total monthly rainfall in winter, but this relation was less pronounced in summer (Struyf *et al.*, 2004). At the upward boundary (Melle, km 158) the same seasonal pattern of discharge was noted as for Schelle.

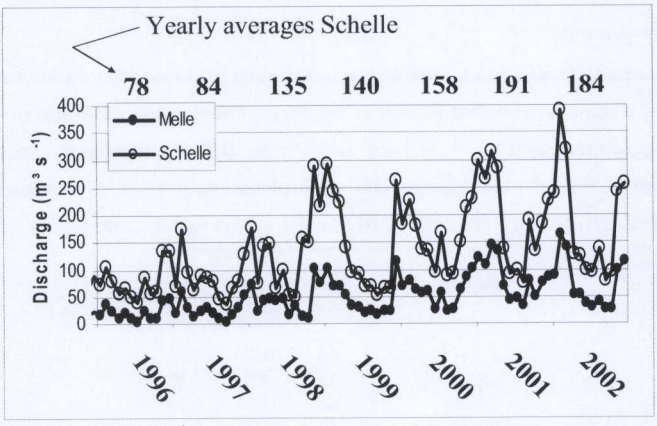


Fig. 3.2: Discharge in the Scheldt estuary at the upward boundary (Melle) and at the mouth of the Rupel tributary (Schelle)

3.3.2 Parameter patterns

Temperature ranged between 0°C (in January 1996 with pack ice drifting in the estuary.) and 24°C in August 1997 and showed an obvious seasonal pattern (Fig. 3.3). Applying the Venice

System (1958) the polyhaline zone (18-30 PSU) was observed to range from the mouth of the estuary to the zone between approximately km 20 (winter 2001) and km 55 (summer 1996) (Fig. 3.4). An oligohaline zone (0.5-5 PSU) was situated roughly upward Antwerp (km78), with downstream extensions of over 20 km during peaking discharge. Sporadically 'true' limnetic conditions (0-0.5 PSU) appeared. The oligohaline and limnetic zones together will further be referred to as the 'freshwater part' of the estuary. The mesohaline zone (5-18 PSU), further called brackish part, was highly variable in space and time, stretching over a range of 20 to 40 km, and shifting according the changes in the oligohaline and the polyhaline zones. Between 1996 and 2001 isosalinity lines generally shifted I downstream direction over more than 20 km. For all stations, the slopes of the linear trends of salinity vs. discharge (data for the whole sampling period) were plotted versus station position along the river (Fig. 3.5). The linear trends were all negative and significant (data not shown). The results show that the effect of discharge on salinity is in general most pronounced around km 42 (most negative slope), *i.e.* at the transition of the polyhaline to the mesohaline zone.

Values of pH were confined in the alkaline range (Fig. 3.6). Lowest values were measured predominantly in the zone between km 70 and km 100, *i.e.* in the downstream part of the oligohaline zone.

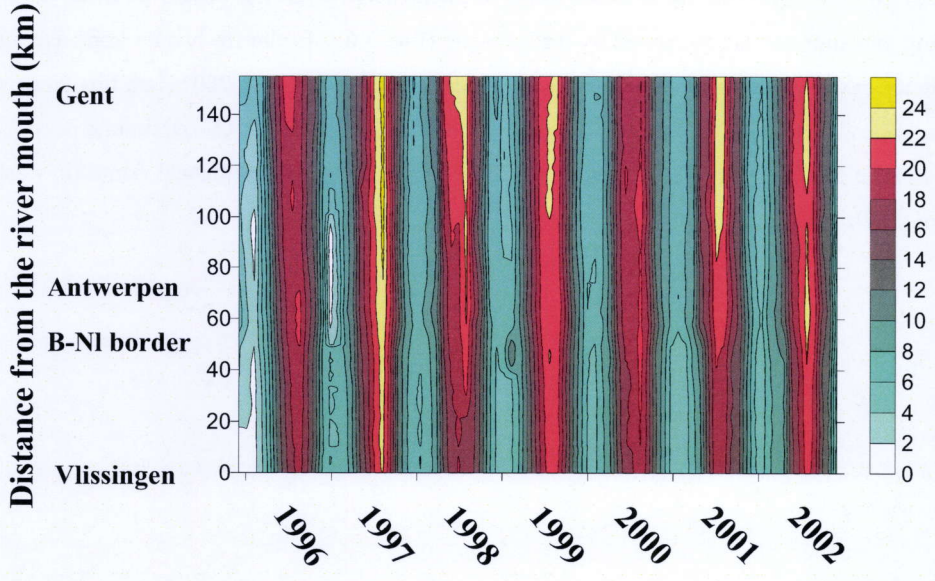


Fig. 3.3: Temperature along the estuarine axis of the Scheldt, unit: °C

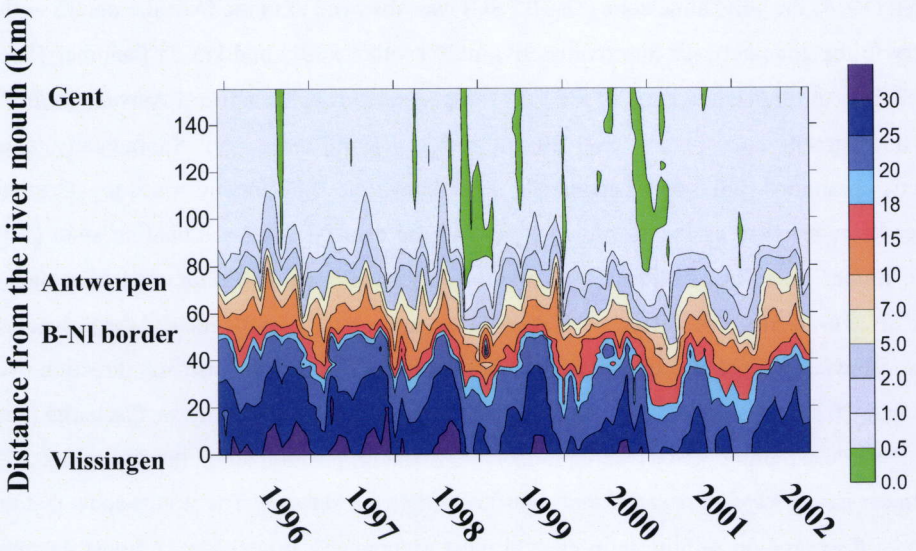


Fig. 3.4: Salinity along the estuarine axis of the Scheldt, unit: psu

Oxygen concentrations are generally low in the Sea Scheldt and increase quickly near the Dutch-Belgian border, downstream km 70 (Fig. 3.7). During winter O_2 concentrations increased in the Sea Scheldt, whereas in the Westerschelde supersaturation was noted during spring and summer, accompanied by a rise of pH (Fig. 3.6). In the freshwater zone average summer oxygen concentrations improved considerably from 1996 to 2001, and this increase related positively with discharge (Struyf *et al.*, *op. cit.*). The worst O_2 conditions persisted around the mouth of the Rupel tributary (km 92), carrying mostly untreated domestic waste from the Brussels region.

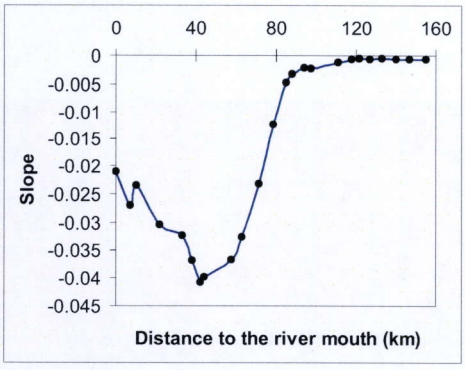


Fig. 3.5: Slopes of the linear trend lines of salinity vs. discharge plots over the longitudinal gradient. Salinity – discharge plots were made for every sampling station and included all data of the studied period.

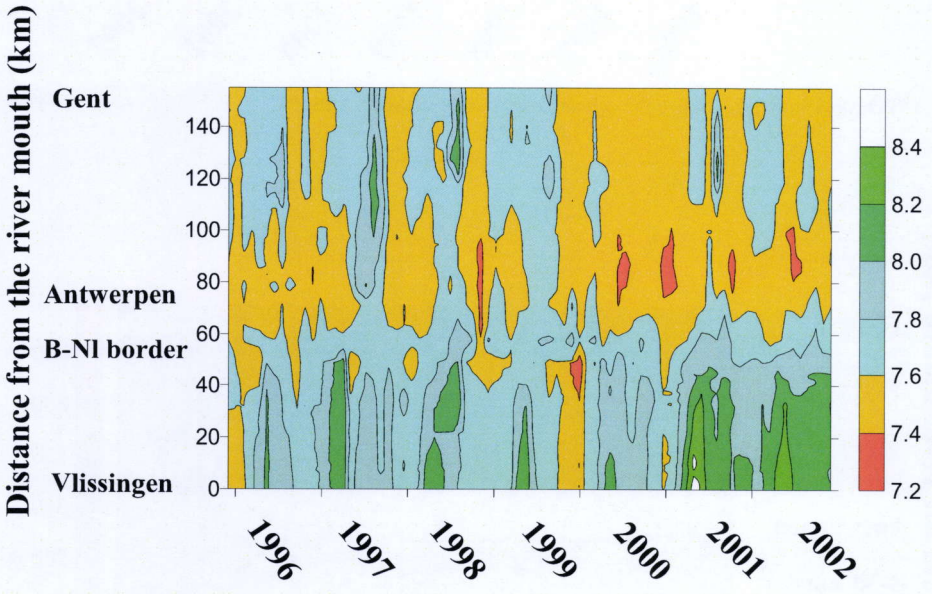


Fig. 3.6: pH along the estuarine axis of the Scheldt

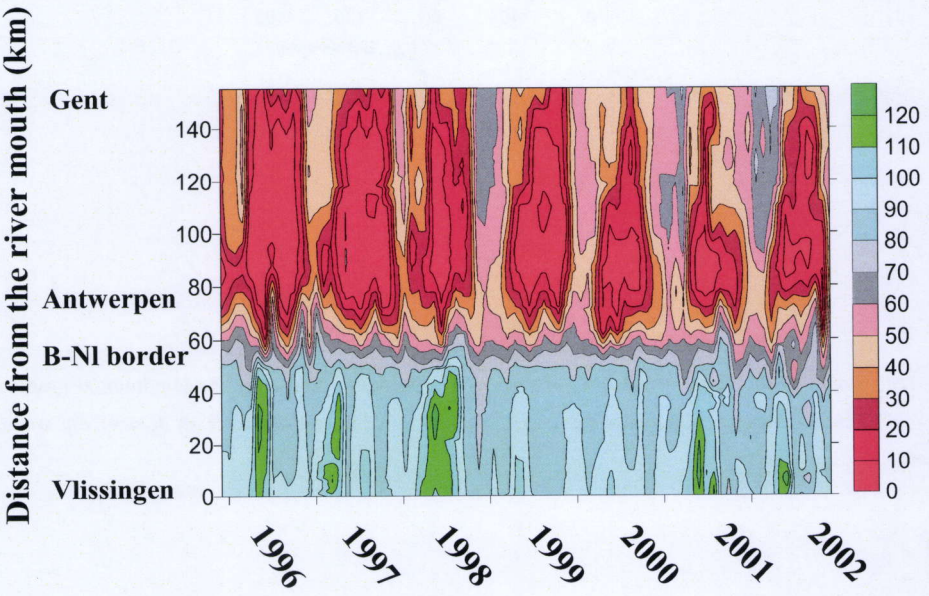


Fig. 3.7: Oxygen saturation along the estuarine axis of the Scheldt, unit: %

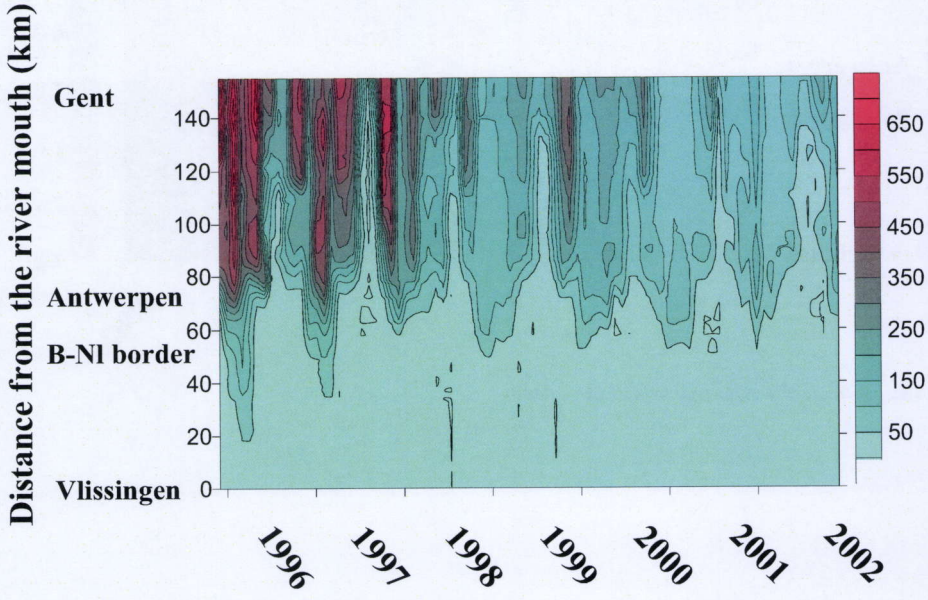


Fig. 3.8: Ammonium along the estuarine axis of the Scheldt, unit: µmol N L^{-1}

In the Westerschelde NH_4^+-N concentrations dropped almost to zero, a phenomenon that was extended in summer upstream until Antwerp (km 78) (Fig. 3.8). In winter ammonium concentrations were much more elevated in the Sea Scheldt, but a significant decrease was observed from 1996-1997 to 2001-2002. This difference was more pronounced for winter compared to summer (Struyf *et al.*, *op. cit.*). Year round nitrate concentrations were significant even downstream the Dutch-Belgian border (km 58) (Fig. 3.9). Yearly maxima, reached in winter time, slightly dropped during the study period, but seasonal differences became smaller and in 2001 and 2002 nitrate concentrations remained high throughout the year; in 2001-2002 nitrate concentrations at the river mouth were higher than in 1996-1997. Nitrite peaked during summer in the freshwater part, while it did during winter in the saline part, although in the latter concentrations were very low (Fig. 3.10). Extreme nitrite values were recorded in the summer of 2001, coinciding with extreme Chl a (Fig. 3.11) contents. In contrast to O2, the TDIN pattern did not reflect a direct influence of the Rupel tributary (Fig. 3.12). TDIN exhibited a clear longitudinal gradient, with maximal values in the freshwater part recorded during winter of 1996 and 1997 when discharge was low. No such variability was observed near the river mouth.

A distinct zone with high orthophosphate (DRP) concentrations was apparent upstream km 90-100 (Fig. 3.13). DRP and total P concentrations dropped significantly in the region where higher SPM concentrations prevailed (km 100-120) (Figs. 14 & 15). In the outer reaches of the estuary DRP minima coincided with phytoplankton blooms during spring or summer (Fig. 3.11).

The pattern of SPM was quite patchy (Fig. 3.14), showing in general much higher concentrations in the Sea Scheldt than in the Western Scheldt. The seasonal variations are due to a complex of factors, such as the river discharge (transport, shift of the turbidity maximum), temperature (biological activity, climatologic factors) and land erosion (terrestrial input of fine sediments). The pattern of SPM is discussed in further detail in Chen *et al.* (2004). For the whole estuary there was a close linear relationship between SPM and POC (Fig. 3.16) (POC = 0.052 SPM + 0.190, R^2=0.71, d.f.=1636, F=3946, p=0). BOD was not measured in the Westerschelde proper, but from Fig. 3.17 it is clear that BOD decreased with increasing salinity, as was also observed for DOC (Fig. 3.18). However, there was no significant relationship between BOD and DOC. High BOD values were observed in 1996-1997, while DOC concentrations remained rather constant over the years.

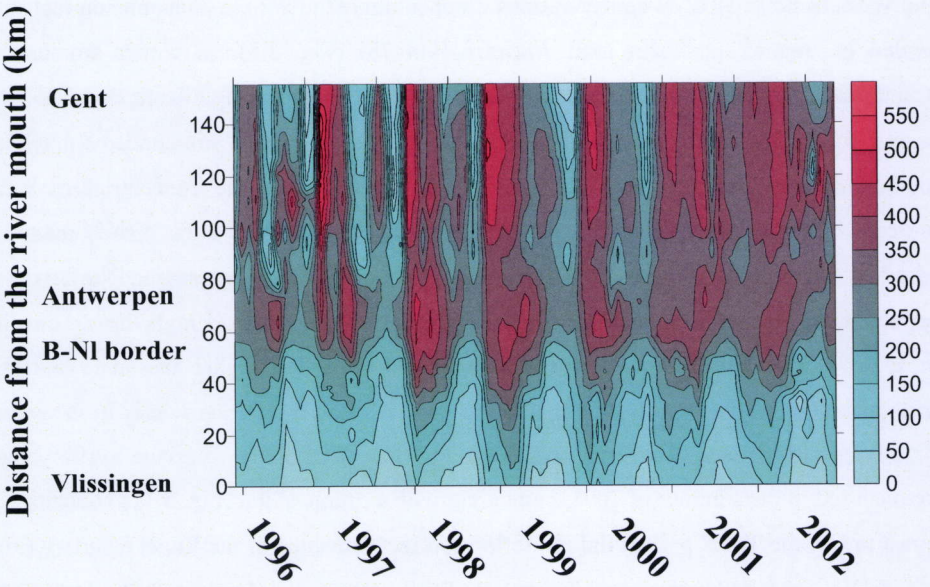


Fig. 3.9: Nitrate along the estuarine axis of the Scheldt, unit: µmol N L^{-1}

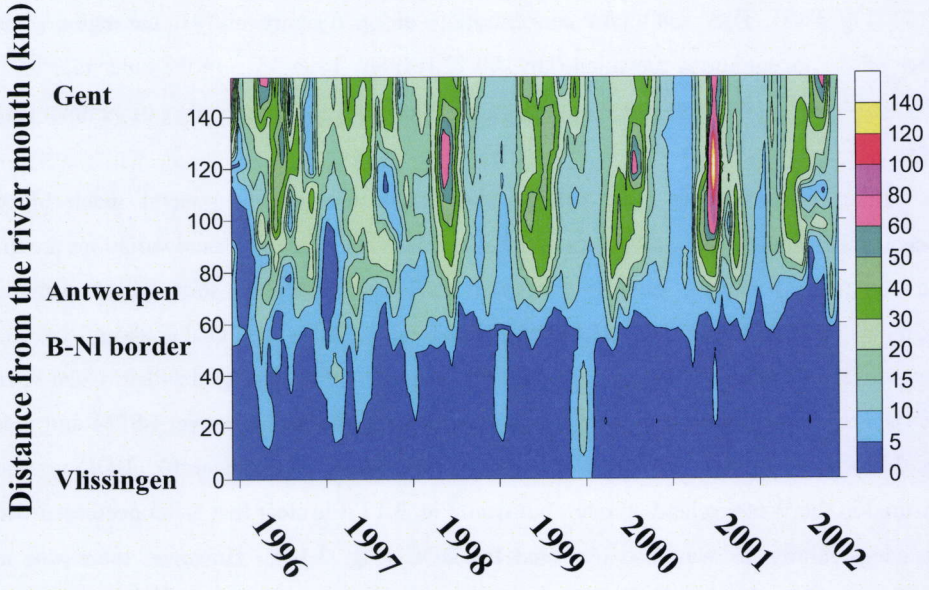


Fig. 3.10: Nitrite along the estuarine axis of the Scheldt, unit: µmol N L^{-1}

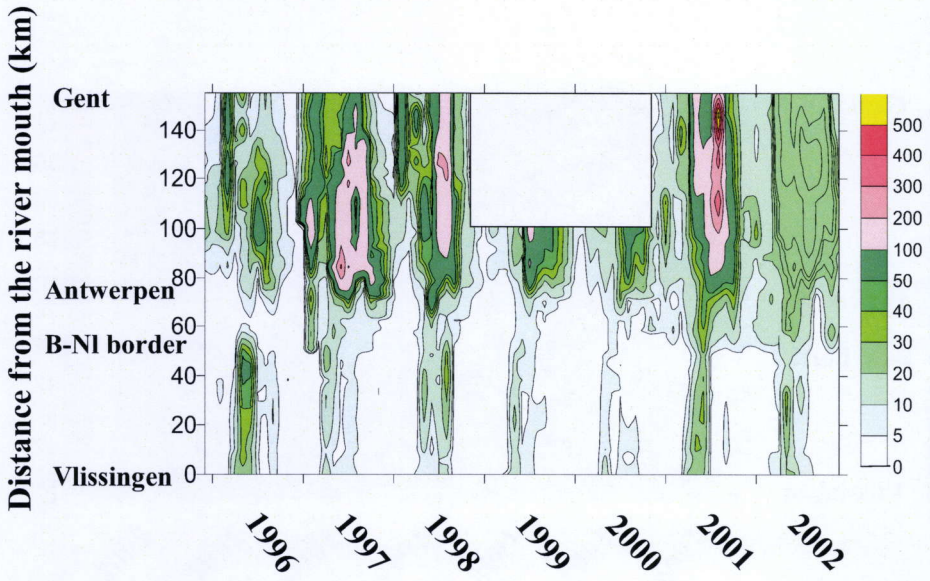


Fig. 3.11: Chlorophyl a (Chl a) along the estuarine axis of the Scheldt, unit: μg L^{-1}

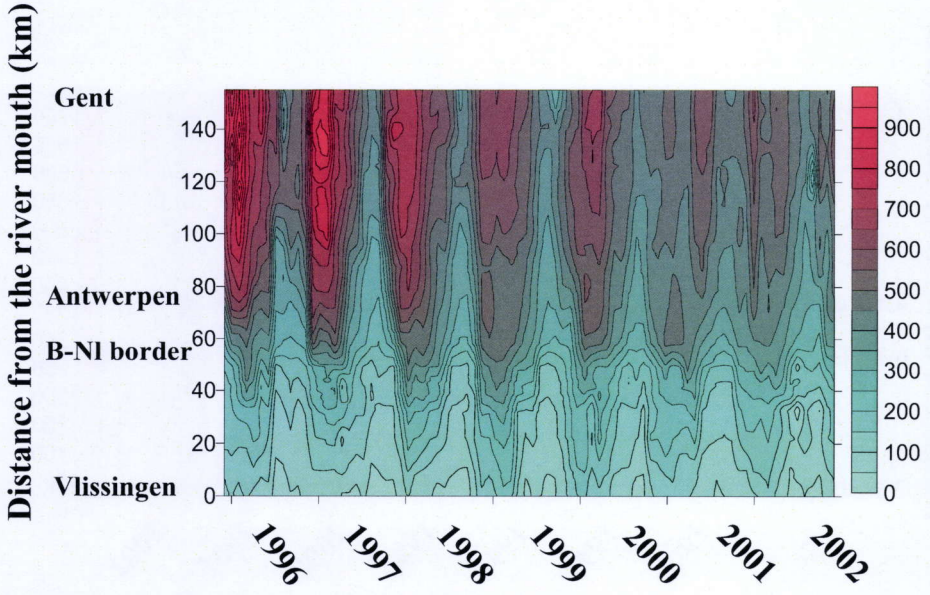


Fig. 3.12: Total dissolved inorganic nitrogen (TDIN) along the estuarine axis of the Scheldt, unit: μmol N L^{-1}

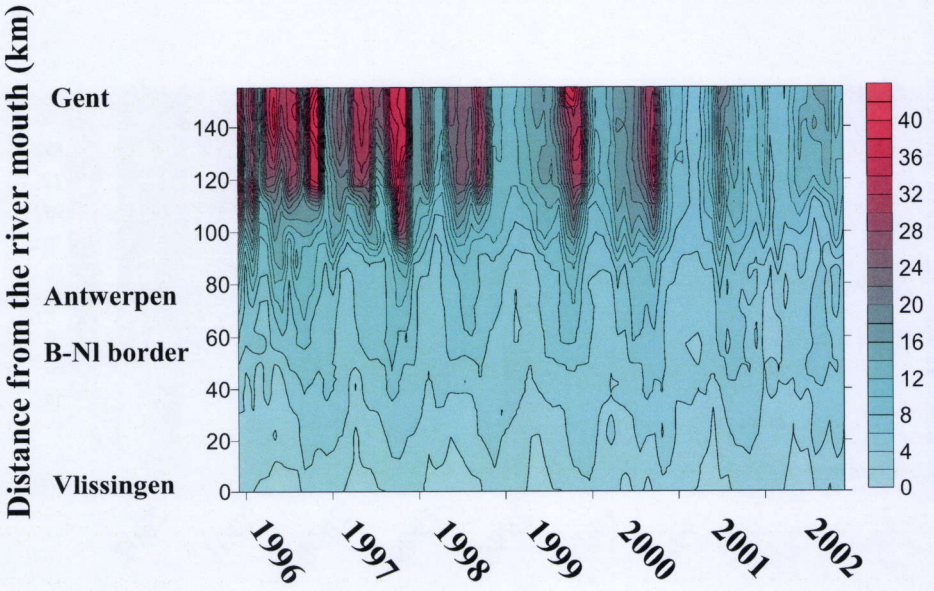


Fig. 3.13: Orthophosphate (DRP) along the estuarine axis of the Scheldt, unit: µmol P L^{-1}

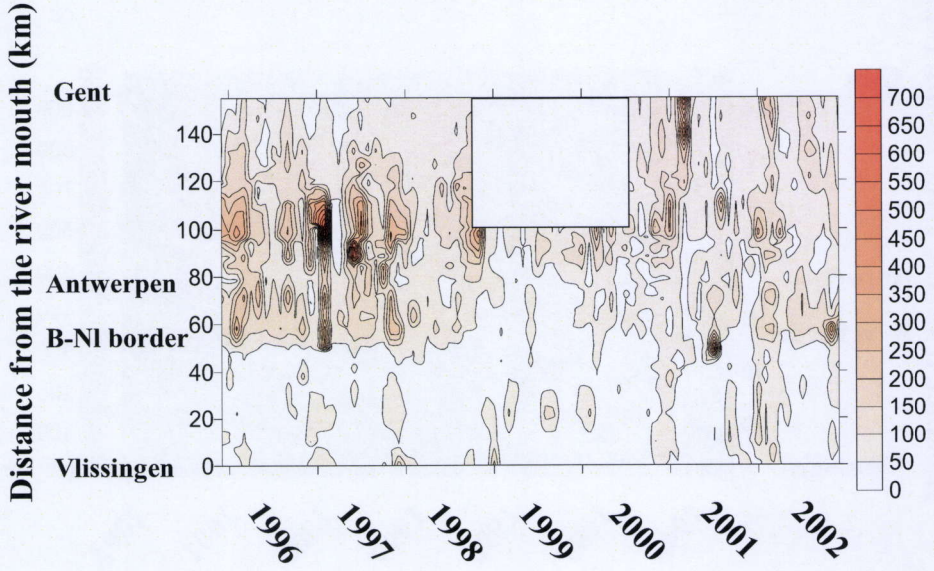


Fig. 3.14: Suspended particulate matter (SPM) along the estuarine axis of the Scheldt, unit: mg L^{-}

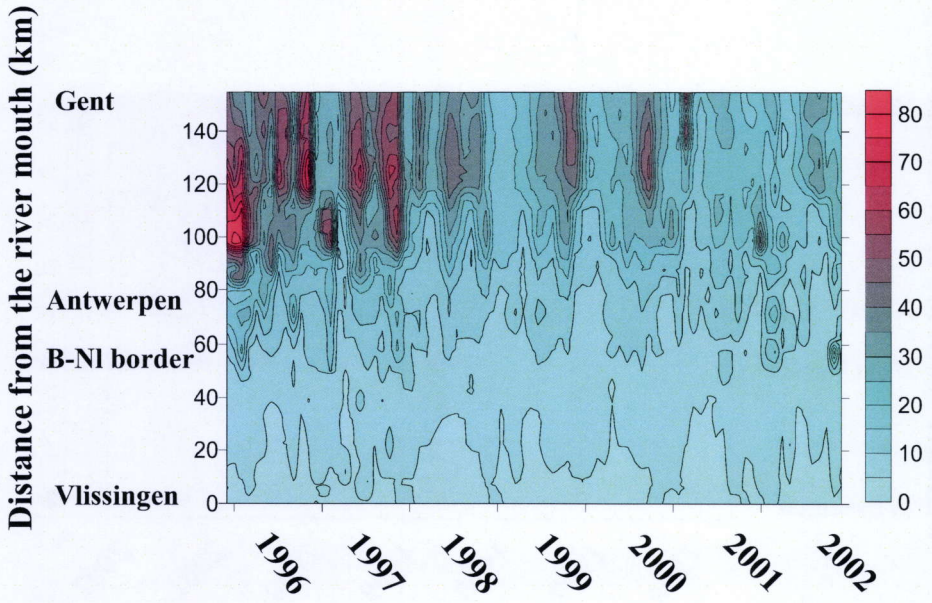


Fig. 3.15: Total phosphorous along the estuarine axis of the Scheldt, unit: µmol P L^{-1}

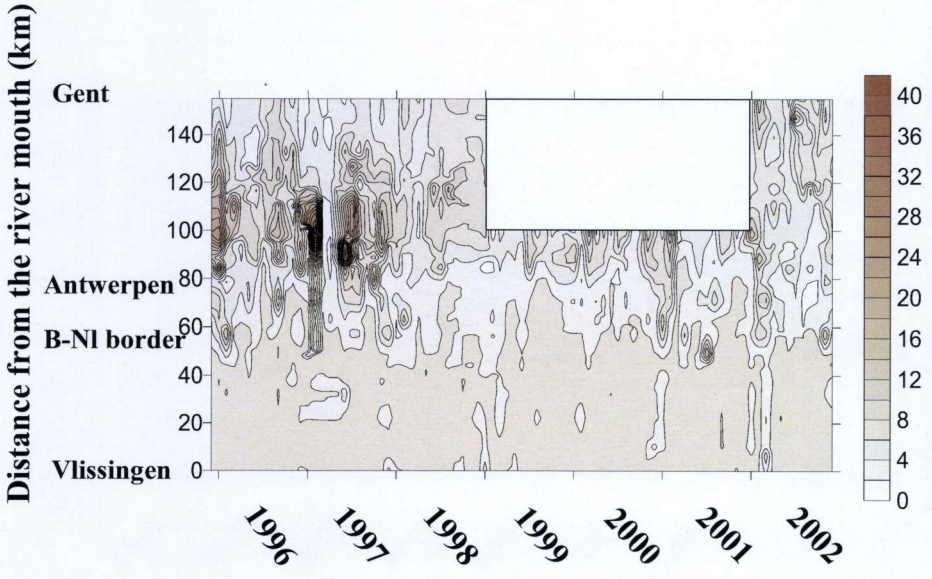


Fig. 3.16: Particulate organic carbon (POC) along the estuarine axis of the Scheldt, unit: mg C L^{-1}

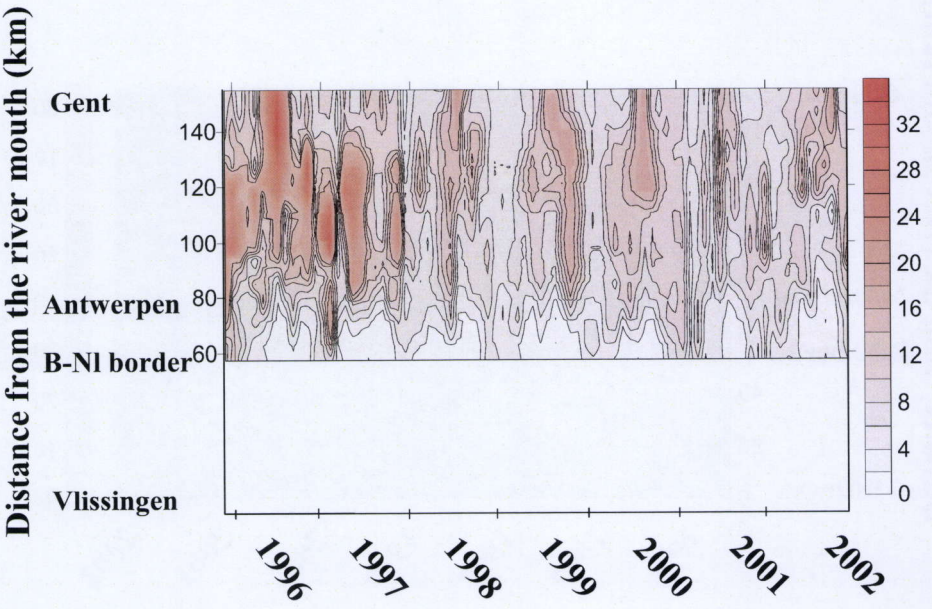


Fig. 3.17: Biological oxygen demand (BOD) along the estuarine axis of the Scheldt, unit: mg L^{-1}

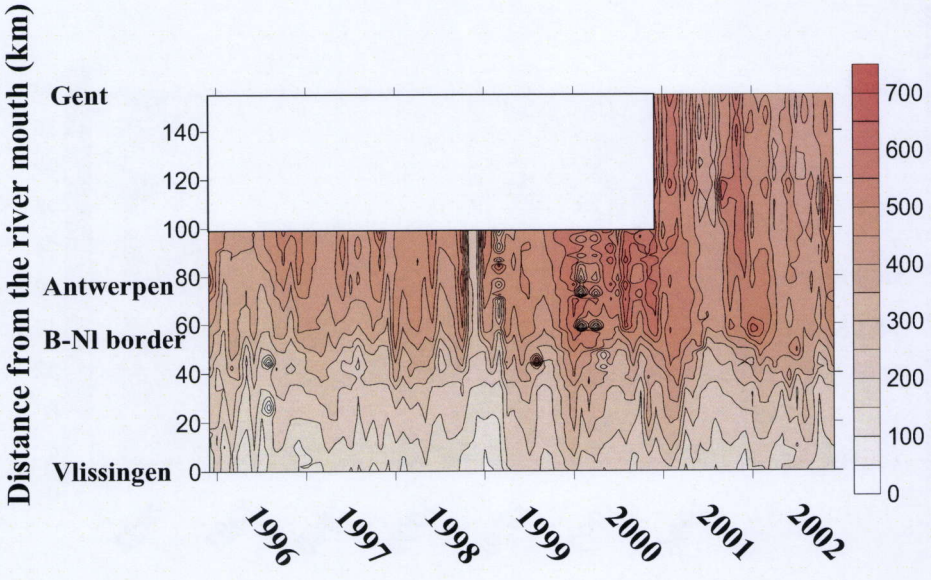


Fig. 3.18: Dissolved organic carbon (DOC) along the estuarine axis of the Scheldt, unit: µmol C L^{-1}

Chl a concentrations were highest in the freshwater part, decreased in the brackish part, and increased again in the marine part (Fig. 3.11). Chl a showed peaks during spring and summer, especially in the freshwater part. No clear trend was observed during the study period, but in 2002 the Chl-a concentrations in the freshwater part were relatively low. The pattern of DSi showed a distinct decrease during summer compared to winter (Fig. 3.19). Winter DSi concentrations remained rather constant over the years, while summer concentrations greatly increased over the study period (Struyf *et al.*, *op. cit.*).

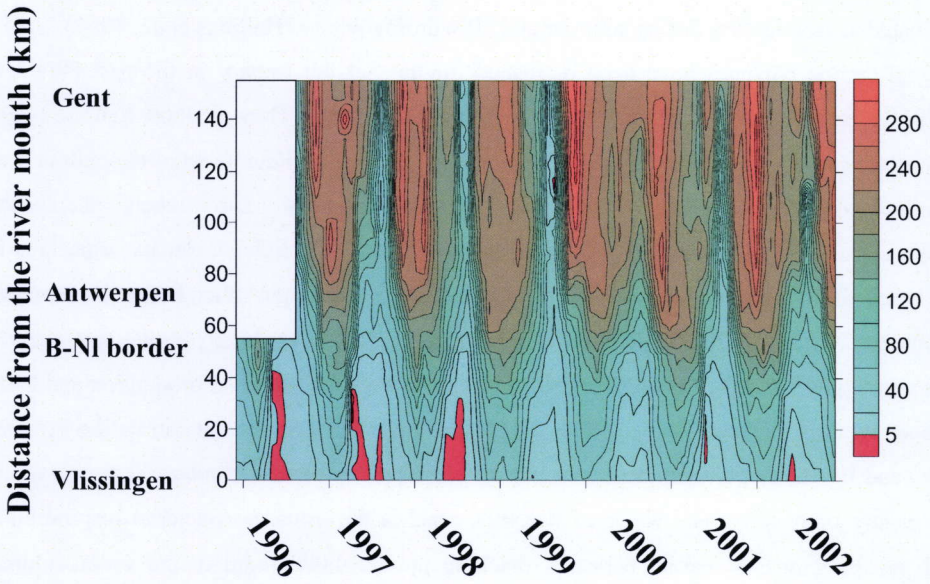


Fig. 3.19: Dissolved silica (DSi) along the estuarine axis of the Scheldt, unit: µmol Si L^{-1}. Concentration contour fills lower than 5 µM Si are highlighted in red, indicating possible limitation for diatoms (Van Spaendonk *et al.*, 1993).

3.4 Discussion

The high spatial resolution and the monthly measurement frequency in this study allowed for a detailed description of the spatial and temporal variability of the water quality along the whole salinity gradient of the Scheldt estuary. For most parameters, spatial gradients were obvious, reflecting the downstream increasing influence of the seawater entering the estuary from the North Sea during each tide. Seasonal and inter-annual variability was large, mainly reflecting climatic conditions such as fresh water run off and temperature variations.

3.4.1 Carbon and oxygen

The phytoplankton contribution to POC estimated from stable carbon isotope data of SPOM and DIC, was estimate to vary between 17 and 65%, during periods of algal bloom (Hellings *et al.*, 1999). Slightly lower values, from 10 to 30 %, are reported by Muylaert *et al.* (pers.com.), as deduced from phytoplankton productivity studies (Muylaert *et al.*, 2004). Since the contribution of terrestrial vegetation to POC was estimated at 2 to 10% (Tackx *et al.*, 1999????), the anthropogenic fraction of the POC in the freshwater part can therefore be estimated at around 45% during summer and 80% during winter (Hellings *et al.*, 1999).

Several carbon balances have been published for the Scheldt estuary in the past (Wollast, 1978; Soetaert & Herman, 1995a; Frankignoulle *et al.*, 1996). They all show that the major part of the carbon input in the estuary does not reach the sea and that most of the carbon load is processed within the estuary itself. Only the most refractory fraction reaches the coastal waters (Soetaert & Herman, 1995a). Bacterial production in the Scheldt estuary, especially in the brackish and freshwater part, showed highest values amongst other European estuaries (Goosen *et al.*, 1995). Especially around the mouth of the Rupel tributary strong heterotrophy was noted (Heip *et al.*, 1995). Although a correlation between bacterial production and DOC hs been reported (Goosen *et al.*, 1995), the present study did not reveal a correlation between DOC and BOD. The oxygen depletion is most prominent at the Rupel mouth (km 90), where the mostly untreated waste water of Brussels, reaches the estuary. Bacterial respiration is high resulting in CO_2 partial pressure, reaching up to 10,000 µatm in the water column, corresponding to more than 2,500 % oversaturation (Frankignoulle *et al.*, 1996). These were the highest values of several European estuaries (Frankignoulle *et al.*, 1998), the freshwater part of the Scheldt not even being included. For the freshwater part, Hellings *et al.* (2001) calculated even higher CO_2 partial pressures exceeding those in the brackish zone by about about 50%. Hence it appears that the fate of most of the carbon input to the estuary is outgassing to the atmosphere.

The enormous detritus load and coupled bacterial production seems to form a dead end in the food chain. So far, neither detritus nor bacteria were proven to constitute an important nutrient source for higher trophic levels, considering such facts as the importance of phytoplankton for macrobenthic suspension feeders and of microphytobenthos for deposit feeders (Herman *et al.*, 2000), the feeding selectivity of zooplankton (Tackx *et al.*, 2003), the lesser importance of grazing on bactivorous ciliates than on herbivorous ciliates (Hamels *et al.*, 1998), or the relationship between system averaged macrozoobenthic biomass and system

averaged phytoplankton productivity (Herman *et al.*, 1999). Thus, it would appear that the anthropogenic carbon load does not benefit to overall estuarine ecological functioning as it does not really lead to enhanced productivity of the higher trophic levels.

3.4.2 Nitrogen

In the fresh water part the relative contribution of ammonium to the total N pool represented more than 50% during winter (January – February). At the Dutch-Belgian border (brackish part) nitrate contributed always, except in the low discharge winter periods of 1996 and 1997, more than 70% of total N. At the transition from the freshwater to the brackish zone a peak of nitrification activity was measured (de Bie *et al.*, 2002) which could explain the observed pH minima in this zone. Nitrification activity declined in downstream direction, probably because of ammonium limitation, while in the upstream part low oxygen concentrations appear to control nitrification, as deduced from modeling (Billen, 1975; Billen and Somville, 1982). As oxygen concentrations increased since the second half of the seventies (trend at the Dutch-Belgian border), the nitrification front moved upstream and intensified to become the process with the greatest impact on the N-load (Soetaert and Herman, 1995b; Regnier *et al.*, 1997). More than one third of the oxygen consumption was then due to nitrification (Ouboter *et al.*, 1998).

Nitrate is not only produced in the estuary, it is also removed. In the early eighties, a first mass balance for nitrogen (N), based on data for the period 1975 to 1983, showed a reduction of the N-load of 40 to 50% in the estuary, mainly as a result of denitrification (Billen *et al.*, 1985). Modeling by Soetaert & Herman, (1995b) showed that ten years later the N-output towards the sea had doubled. and confirmed that denitrification decreased due to the improved oxygen conditions. This phenomenon became locally known as the paradox of the Scheldt estuary.

Denitrification in the Scheldt was found to be most important in the pelagic compartment (Soetaert & Herman, 1995b). Pelagic denitrification however is subject to changes in residence time of the water in the estuary, itself largely controlled by discharge. The nitrogen fraction that was denitrified could be predicted from the freshwater residence time for several estuaries (Dettmann, 2001). Soetaert & Herman (1995c) modelled that the difference between a typical winter and summer discharge caused a difference of residence time in their most upstream studied compartment (*i.e.* around Temse; km 100-108): In summer the residence time was about 30% less than in winter. Further upstream the impact of discharge

is bigger, so the effect on residence time must be greater. The average summer discharge (June – August) in 2000 (118 $m^3.s^{-1}$) was double of that in 1996 (56 $m^3.s^{-1}$). According Soetaert & Herman (*op cit.*) this implies that in the fresh water part the nitrogen turnover due to pelagic denitrification had to be at least 20% lower in 2000 than in 1996. This is not reflected in the profile of TDIN, but the effects of discharge on N-nutrients are multiple (Struyf *et al.*, 2004). A discharge dependent increase of the nitrate and TDIN load in the fresh water part indicated increased input in the estuary proper, buth this effect was partly masked by dilution. So far an increased output to the coastal zone is not clear. Apart from the pelagic volume aspect of denitrification there is also a surface effect. For a tidal mudflat in the brackish zone near the Dutch-Belgian border Middelburg *et al.* (1995) calculated that 55% of the total N flux from water column to sediments was denitrified. Comparison with Soetaert & Herman (1995b) leaded to the conclusion that tidal areas between the Vlissingen and Temse (km 110) accounted for 14% of the total N removal in that part of the estuary. In the fresh water zone more intense denitrification values were found (Van Damme *et al.*, in prep.), which is in accordance with Rysgaard *et al.* (1999) who revealed a clear negative relationship between denitrification and salinity. In tidal marshes the flux of nitrate from the water into the sediment appears to be the limiting factor for denitrification, while it is consistently enhanced by bioturbation (*e.g.* Chatarpaul *et al.*, 1980; Pelegri and Blackburn, 1995). Extreme densities of Oligochaetes are reported for the the Scheldt estuary (Seys *et al.*, 1999) and it is therefore likely that these will have a significant effect on dentitrification. In contrast, recent results for a whole ecosystem ^{15}N-ammonium labeling experiment in a fresh water marsh at Tielrode (km 104) indicate that about half of the retained ammonium label was nitrified, while denitrification was of minor importance compared with nitrification (Gribsholt *et al.*, in prep.). Denitrification in the root zone of marsh plants proved to be much less than was indicated by the concept of Reddy *et al.* (1989) and was only enhanced at the end of the growth season (Starink *et al.*, in prep.). Based on these different observations the hypothesis can be put forward that denitrification is relatively more important in mudflats than in marshes, while in the latter nitrification largely exceeds denitrification. Nitrite concentrations are well above 0.64 µM, the Flemmish standard for fish water. While the toxic action of nitrite on fish is incompletely known, long exposure to sublethal concentrations of nitrites was reported not to cause much damage to fish (Svobodova *et al.*, 1993). The LC50 can be influenced by various factors of which salinity is an important one. Minimal Cl/NO_2^-N ratios of 8 to17 (expressed as mg/mg) have been recommended for fresh water and these

conditions were met in the Scheldt throughout. Although a major fish kill was spotted during the September 2002 cruise, this coincided with relatively low nitrite concentrations. In contrast, during summer 2001 when nitrite concentrations peaked, no fish kill was observed.

3.4.3 Phosphorus

Phosphorus (P) is a reactive element and its chemistry in aquatic systems is complex (Corell, 1998). In the Scheldt estuary P received less attention than N, probably because in coastal waters, particularly in the Dutch coastal zone, N and not P have been reported as limiting nutrient for phytoplankton (Peeters and Peperzak, 1990; Billen, 1993). Within the Scheldt estuary phytoplankton N:P ratios generally exceeded 16, indicating a surplus of N on P, although both nutrients were amply available (Van Spaendonk *et al.*, 1993; Kromkamp *et al.*, 1995). Nevertheless, elsewhere in this special issue, Billen *et al.*, (2004) discuss indications that nutrient limitation might have shifted from N to P.

In the Western Scheldt, particle-bound P was dominated by organic P (Zwolsman, 1994). Up till Temse in upstream direction, , Fe-bound P was the major particulate P carrier (detailed data on P speciation further upstream are lacking). The Elbe estuary showed an similar distribution of P species (Van Beusekom & Brockmann, 1998). In the freshwater part, the more complex seasonal pattern of P suggests interaction between a physicochemical buffering mechanism, biological processes and factors controlling input from the river basin (Wollast, 1982; Boderie *et al.* 1993; Zwolsman, 1994).

Orthophosphate and total P are decreasing since the peak concentrations in the seventies (Van Damme *et al.*, 1995), although concentrations today are still one to two orders of magnitude larger than values expected for pristine conditions (Froelich, 1988). The decline in phosphate is attributed to the banning of phosphate based detergents (Zwolsman, 1994), improved agricultural practice and progressive industrial and municipal water treatment. Furthermore, from 1996 to 2001 increasing discharge diluted the P-load in the freshwater part (Struyf *et al.*, 2004), but this effect was not observed further downstream. At Antwerp the total P-load was even smaller than the one in Rupel and Upper Scheldt. This is a confirmation that P must be retained within the estuary. Thus, the seasonal pattern and trend indicate that in the downstream part of the estuary P is mainly removed by phytoplankton, while more upstream physicochemical processes are the dominant processes.

3.4.4 Phytoplankton

Light is the predominant limiting factor for phytoplankton growth in practically the entire Scheldt estuary, nutrient limitation being almost non-existent (Van Spaendonk *et al.*, 1993; Soetaert *et al.*, 1994; Kromkamp *et al.*, 1995; Cloern, 1999; Muylaert *et al.*, 2000a). Despite lower concentrations of SPM in the Westerschelde, Chl a concentrations are lower than in the freshwater part, probably due to differences in mixing depth – photic depth ratios. Despite the light limitation, high anthropogenic inputs of N and P can eventually induce silica limitation and a subsequent dominance of non-diatom phytoplankton over diatoms, especially.in coastal zones (Schelske *et al.,* 1983; Smayda, 1990; Smayda, 1997). At the mouth of the estuary limitation of DSi for diatoms was evidencec from several approaches: (1) summer, N:Si nutrient ratios < 1 (Van Spaendonk *et al.*, 1993; Kromkamp *et al.*, 1995); (2) modelling indicates a DSi limitation of maximum 15% (Soetaert *et al.*, 1994); (3) low spring DSi concentrations compared to a half-saturation constant, estimated at 1 – 5 µM (Van Spaendonk *et al.*, 1993). While large amounts of DSi are biologically removed during summer, this element behaves conservatively in wintertime (Boderie *et al.*, 1993; Zwolsman, 1994). Silica loads at the mouth of the estuary were related with discharge (Struyf *et al.*, 2004). As DSi predominantly originates from biogeochemical reactions which set free dissolved silica from alkali and aluminosilicate minerals (Correll *et al.*, 2000), increasing discharge resulted in increased Si input in the estuary. Furthermore, peaking discharge had a negative influence on DSi uptake by diatoms since estuarine phytoplankton communities were washed away. This, however, is not reflected in the chlorophyll concentration pattern since the estuarine phytoplankton community was replaced with one of riverine origin, not adapted to conditions prevailing in the brackish zone (Muylaert *et al.*, 2001).

Phytoplankton primary production in estuaries plays an essential role in element cycling, water quality, and food supply to heterotrophs. As phytoplankton in the Scheldt is highly important for the food web (Herman *et al.*, 1999), it is crucial to know how it is transferred to higher trophic levels. It was estimated that phytoplankton in the Westerschelde might be controlled by grazing (Soetaert *et al.*, 1994), mainly by copepods, dominating the zooplankton community (Soetaert & Van Rijswijk, 1993; Soetaert & Herman, 1994). Tackx *et al.*, (2003) showed for the dominant copepod *Eurythemora affinis*, that 80% of the food required to achieve optimal physiological condition could be obtained via grazing if 3% of the POC load consists of phytoplankton carbon (Phyto-C), conditions which might not be fulfilled during winter and when turbidity peaked. In the freshwater part Rotifers are the dominant

zooplankton species, and these can withstand low oxygen conditions (Soetaert & Van Rijswijk, 1993; Muylaert *et al.*, 2000b). Because of their feeding characteristics it is unlikely they seriously reduce phytoplankton stocks (Muylaert *et al.*, 2000b). Such as for phytoplankton, the salinity gradient also turns out to be lethal for both saline and freshwater zooplankton communities.

3.4.5 Implications for estuarine management

Although a serious attempt has been made to integrate two international monitoring programmes, it is clear that further efforts are required, *e.g.* through a further standardization of the methods and the parameters measured (*e.g.* adding BOD measurements to the CEME monitoring). A seven-year study period is of course rather limited, and we will need continuous monitoring data that span periods of decades, to be able to untangle the multiple variability mechanisms and to separate anthropogenic influences from natural variability in order to understand the effects of our current use of water resources. Despite this relatively short study period some implications for management are obvious.

The Scheldt estuary is heavily burdened with organic carbon and nutrient inputs. Concerning carbon efforts focus should be on the reduction of the anthropogenic immission into the estuary. In the freshwater part a complete reduction of anthropogenic carbon immission would lead to about a 10% decrease of the SPM load during phytoplankton bloom, stimulating in that way estuarine primary production. Bacterial respiration consumes a major amount of the available oxygen. As the main source of oxygenation in the estuary is aeration (Soetaert & Herman, 1995a), creation of areas with high surface/depth ratios is advised in the zone where oxygen concentrations are minimal.

The waste water treatment plants of Brussels are nowadays under construction. It is believed that once the waste load of this major source of pollution is treated, the water quality of the Scheldt will improve consistently. However, a risk of generating a new carbon load exists. Indeed, since the water coming from Brussels via the Zenne has about 30 km to flow before it reaches the Scheldt, diffuse input of nitrate from surrounding agricultural terrain to the rehabilitated tributary would favour phytoplankton growth and induce again excessive carbon load.

Management can influence removal of nitrogen in the estuary. Expansion of intertidal or flooding areas contributes both to the reactive denitrification surface and to an increase of storage capacity and hence would increase N_2-efflux to the atmosphere. It is expected that the

reactive surface will gain importance on the pelagic aspect as restoring oxygen conditions will subdue pelagic denitrification even further as it has already done.

Billen & Garnier (1997) stated that phosphate removal through water treatment is essential to prevent coastal eutrophication once the N-problem is under control. As water treatment is still expanding throughout the drainage basin, it is expected that the decreasing temporal trend for P will persist.

It is important to enhance phytoplankton growth provided that primary production is channelled to higher trophic levels. For phytoplankton, a combination of measures towards attenuation of dynamics, both of tidal dynamics and wash outs, and measures to reduce nutrients and enhance silica cycling is the best option. Silica cycling can be enhanced by creation of tidal wetlands.

Before all else higher trophic levels require improved oxygenation degree, especially in the Sea Scheldt. Filter feeders (zooplankton and macrobenthic filterfeeders) deserve priority because they pass on the primary production towards higher levels in the food web such as fish and birds.

The quantification of the relative importance of the different quality goals mentioned for restoration of ecological estuarine functioning remains a scientific challenge.

Acknowledgements

The OMES monitoring was funded by the Flemisch Administration for Waterways and Maritime Affairs, division Zeeschelde. We thank the Fund for Scientific Research for funding the Scientific Community 'Ecological characterization of European estuaries, with emphasis on the Schelde estuary' (project nr. W 10/5 - CVW.D 13.816), and for funding Dutch-Flemish ecological research projects on the Schelde (project nr. G.0439.02). We thank Lieve Clement and Eva De Bruyn from the "Testing Laboratory for Chemical Water Quality" for their support.

Chapter 4

Possible effects of climate change on estuarine nutrient fluxes: a case study in the highly nutrified Schelde estuary (Belgium, The Netherlands)

Struyf E., Van Damme S. & Meire P.

Estuarine, Coastal and Shelf Science 60: 649-661 (2004)

Abstract

Global change models predict effects of climate change on hydrological regimes at the continental scale in Europe. The aim of this study was to gain a better understanding of the possible effect of changing external forcing conditions on the functioning of estuarine ecosystems. In densely populated areas, anthropogenic nutrient enrichment and consequent alteration of nutrient biogeochemical cycles have already had a big impact on these ecosystems. The average yearly discharge of the upper Schelde estuary increased nearly threefold over the period 1996-2000, from 28 $m^3 s^{-1}$ in 1996 to 73 $m^3 s^{-1}$ in 2000. The continuously rising discharge conditions over the 5-year period were used as a reference situation for possible future effects of climate on ecological functioning through increase of discharge. At high discharges, nutrient (NH_4^+, NO_3^-, dissolved silica and PO_4^{3-}) concentrations in the tidal fresh- and brackish water showed a decrease of up to 50% while total discharged nutrient loadings increased up to 100%. Opposite effects of increasing discharge on NH_4^+-, NO_3^-- and dissolved silica concentrations in summer and winter, resulted in the flattening out of seasonal cycles for these nutrients. Under high discharge conditions, silica uptake by diatom communities was lowered. Dissolved silica loadings to the coastal area increased concurrently with total silica loadings upstream. Salt intrusion to the marine parts of the estuary decreased. This

resulted in a downstream shift of the salinity gradient, with lower salinity observed near the mouth. As a result, TDIN-, NO_3^-- and dissolved silica concentrations doubled at the mouth of the estuary.

4.1 Introduction

Coastal zones and shallow marine areas are among the most productive systems in the world (Mann, 1988; Glantz, 1992). They form the main fishery grounds on Earth (Postma & Zijlstra, 1988; Sherman *et al.*, 1991). One of the major worldwide problems, in densely populated areas, is the eutrophication of these estuarine and coastal waters (Nixon, 1990; Gray, 1992; Doering, 1996; Boesch 2002). For most temperate estuaries and coastal ecosystems, N is the element most limiting to primary production and most responsible for eutrophication (Howarth, 1988; Howarth *et al.*, 1996, Nixon *et al.*, 1996). Since the reduction of phosphorus inputs from polyphosphate-containing washing powders, phosphorus concentrations in estuarine environments have decreased, while nitrate concentrations remained high (Van Damme *et al.*, 1995; Billen & Garnier, 1997; Zwolsman, 1999). In contrast to N and P, the silica concentration in estuaries is only indirectly influenced by human pollution. Diatom communities require about equal amounts of N and Si. Diatoms are an essential element of coastal water food chains. Increased N-concentrations can lead to a succession from phytoplankton communities dominated by diatoms to phytoplankton communities dominated by species that are not taken up by higher trophic levels (*e.g. Phaeocystis* sp., *Gonyaulax* sp., *Chrysochromulina* sp.) (Schelske *et al.*, 1983; Smayda, 1990; Smayda, 1997). The North Sea, with extensive input of nutrients from rivers (Rhine, Elbe, Schelde) and its isolated nature, has been characterized by increasing eutrophication events (Lancelot *et al.*, 1987; Brockmann *et al.*, 1988; Richardson, 1989; Lancelot, 1995; Ducrotoy *et al.*, 2000).

Coastal zone ecosystems are strongly affected by natural variations in climate (Holligan & Reiners, 1992). Human induced climatic changes can accordingly have a further effect on the ecology of estuarine environments. Regional and global shifts in temperature, changes in cloud cover, increasing or decreasing precipitation regimes and sea level rise are among the most commonly cited alterations due to human impact on the trace gas composition of the atmosphere (Mitchell, 1989, Wigley & Raper, 1992). A reliable forecasting of global change effects on the land-ocean interface is one of the key aspects in the Land-Ocean-Interactions-in-the-Coastal-Zone-programme (LOICZ), a core project of the International Geosphere-Biosphere Programme (IGBP)

(Kondratyev & Pozdnyakov, 1996). Studies, both observational and theoretical, addressing the issue of material fluxes to coastal zones under changing external forcing conditions, have a critical international importance.

Our aim is to focus on the impact of changing hydrological conditions on estuarine water quality and fluxes of nutrients to coastal waters. Generally, in river basins in temperate regions (Belgium, Quebec, Scotland), an increase in discharges and flooding events is predicted (Gellens & Roulin, 1998; Roy *et al.,* 2001; Werritty, 2002). Although different scenarios exist, all scenarios of global change models, at the continental scale of Europe, predict an increased run-off in North and Western Europe (Arnell, 1999). Schelde freshwater discharges could increase up to 28 % during the next century (source: AWZ, Flanders Waterways and Maritime Affairs Administration). Increased precipitation results in a larger proportion of rainfall transferred directly to surface waters by surface run-off as soil storage capacity is exceeded (Wanielista 1990). It is hypothesized that the diffuse nutrient and sediment inputs to the estuary are positively related to the surface run-off and predicted climate change will result in larger loads of nutrients transported towards the estuary.

Higher freshwater discharges can further influence estuarine ecology by decreasing water residence times in the main estuarine channel. The upstream tidal freshwater regions are likely to be most affected by changing freshwater discharges as the impact of marine waters is negligible and advective freshwater flows dominate over dispersive tidal flows. Muylaert *et al.* (2001) have shown how short-term freshets can result in the flushing of entire diatom communities from the freshwater reach. Nutrients and organic material are transferred more rapidly to coastal waters, and important ecological processes (*e.g.* denitrification, nitrification, mineralisation, nutrient uptake) in nutrient cycling have less time to act upon the large volumes of nutrients, which could lead to alterations of fluxes of N, P and Si downstream to coastal waters.

Recent studies have mainly focused on predicting the impact of climate induced hydrological changes on estuarine ecosystem functioning based on modeling different scenarios (Schirmer & Schuchardt, 2001; Nijssen *et al.*, 2001; Justic *et al.* 1997). This study is based on observations made during a period of continuously rising discharge. The period 1996-2000 was characterised by steadily increasing flow conditions in the Schelde estuary, caused by interannual precipitation variability. Detailed time-series of

nutrient concentrations in the marine, brackish and freshwater reaches of the Schelde estuary (1996-2000) where studied under these continuously increasing discharge conditions. Covariation between long-term nutrient and oxygen concentrations on the one hand and freshwater discharges on the other hand was examined using standard least-squares linear regression to assess correlation between nutrient concentrations or nutrient fluxes and discharge.

4.2 Materials and Methods

4.2.1 Study area

The Schelde estuary (Fig. 4.1), located in Northern Belgium (Flanders) and the Southwest Netherlands, has a long history of extensive anthropogenic pollution (De Pauw, 1971; Bakker & Heerebout, 1971; Wollast, 1988; Boderie *et al.*, 1993, Baeyens, 1998). It is known as extremely eutrophic and receives large inputs of nutrients from non-point as well as point sources (Heip, 1988). A large freshwater tidal area characterizes the Schelde. This is approximately situated between Gent (km 155, *i.e.* 155 km upstream of the estuarine mouth) and Temse (km 100). The major tributaries to the Schelde, situated respectively at Dendermonde (120 km upstream the mouth) and at the interface between the freshwater and brackish zone near Temse (100 km upstream the mouth), are the Dender and the Rupel. The Rupel receives large inputs of untreated waste from the city of Brussels.

Upstream of Dendermonde, the tidal freshwater zone is characterized by small channel width (30 m) and depth (5-10 m). The volume of freshwater in this zone is only about 30% of total freshwater volume in the estuary. Consequently, the residence time is short and relatively strongly influenced by freshwater discharges compared to downstream regions (Van Damme, pers. comm.). Changes in freshwater discharge can induce a threefold decrease in residence times in this tidal freshwater (2-6 days).

The brackish part of the estuary is situated between Temse and the Dutch-Belgian border (km 55). The Dutch part of the estuary is the marine region. Dendermonde is situated centrally in the freshwater tidal area. Water quality between Temse and Gent usually shows little longitudinal variation compared to the downstream estuarine

regions (Van Damme *et al.*, 1995). Measurements at Antwerp and Vlissingen represent respectively the brackish and the marine area.

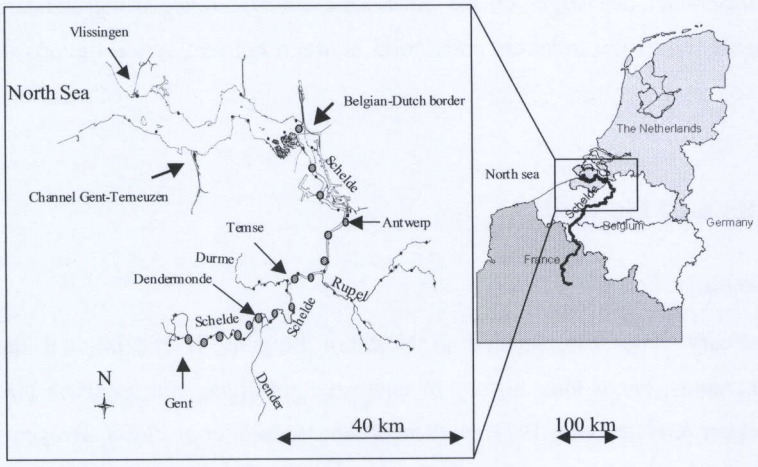


Fig. 4.1: The Schelde estuary and its tributaries; ◦ = monitoring measuring point

4.2.2 Sampling

Between January 1996 and December 2000, surface water samples were taken monthly in the middle of the river from a boat at 16 stations along the longitudinal gradient of the Schelde estuary and in the mouth of the Rupel (from April 1996 on). No samples were taken on the Zeeschelde and Rupel in January 1997 because of ice formation on the rivers. Discharges were measured by AWZ. Discharge of the Bovenschelde (the Schelde just upstream Gent, where tidal influence is stopped by sluices), the Dender and the Rupel was continuously measured, and daily means were calculated. Freshwater discharge at Dendermonde is the sum of discharges of Bovenschelde and Dender, freshwater discharges downstream Antwerp are the sum of Rupel and Dendermonde discharges. The marine (Dutch) estuary is sampled by NIOO-CEME (National Institute of Ecological Research, Centre for Estuarine and Marine Ecology). NIOO-CEME did initially not sample at the same frequency as for the Belgian sampling, especially in winter 1996 and 1997. Some analyzing methods are different for the NIOO-CEME, but intercalibrations were performed to ensure reproducibility.

4.2.3 Analysis

Oxygen was measured *in situ* with a 'WTW OXI 91' oxygen-meter. All other variables were analysed *ex situ* within 24 hours after sampling. Specific conductivity was measured with a 'WTW LF 91' conductivity-meter. Chloride, ammonium (NH_4^+-N), nitrite (NO_2^--N), nitrate (NO_3^--N) and DRP (PO_4^{3-}-P) concentrations were analyzed colorimetrically on a 'Segmented Flow Analyzer Skalar®'. Kjeldahl-N (NH_4^+-N + organic N) and totP were analyzed after digestion in H_2SO_4. Dissolved silica concentration measurement was conducted on an 'Inductively Coupled Plasma Spectrophotometer Iris®'. Silica was monitored since July 1996.

Water quality and discharge data were analyzed for Dendermonde, Antwerp and Vlissingen, respectively 120 km and 80 km upstream of the mouth of the estuary and at the mouth, as well as for the Rupel tributary (Fig. 4.1). Winter and summer were defined as January-March and June-September respectively. These periods were chosen because they show the least intra-annual variation in water quality and low and high chlorophyl a-concentrations (biological activity) respectively (Van Damme, pers. comm.). To measure the influence of discharge on quality trends, it is important to make a seasonal distinction, as nutrient concentrations and discharge show similar seasonal trends.

Discharged loads per time unit (g s^{-1}) were calculated from equation (1):

$$F = Q * s - EA\frac{\partial s}{\partial x} \qquad (1)$$

in which F is flux (mol s^{-1} over cross-surface), Q is freshwater discharge (m^3 s^{-1}), s is concentration (mol m^{-3}), E is dispersion coefficient (m^2 s^{-1}) and A is cross-surface (m^2). This equation is at the basis of the model used in Soetaert & Herman (1985). At Dendermonde and Antwerp, dispersive transport is negligible, discharged loads were essentially calculated by multiplying monthly measured concentration (mg L^{-1}) and monthly averaged discharge (m^3 s^{-1}). A recent standardization study of the dataset within tidal, vertical and longitudinal water quality variation, has shown that measured

nutrient concentrations are very good indicators for conditions throughout the whole month (Van Damme *et al.*, 2005). The consistence of the measuring methods ensures that bias (if present) on calculated loads was similar throughout the study period.

For regression analysis on the concentration and freshwater discharge data, these data were log-transformed (log (x+1)). (Log-transformed concentrations were in mg N L^{-1}, mg P L^{-1}, mg O2 L^{-1}, mg Cl^{-1}, mg Si L^{-1}). This is an effective transformation to normalize estuarine water quality data (Jordan *et al.*, 1991; Doering, 1996).

4.3 Results

4.3.1 Hydrology

The average yearly discharge at Dendermonde showed a large variation from a minimum of 28 m^3 s^{-1} in 1996 to a maximum of 73 m^3 s^{-1} in 2000 (Fig. 4.2a). There was a clear seasonal variation with maxima in winter and minima in summer (Fig. 4.2b). Absolute discharge increase was much higher in winter than in summer (Fig. 4.2c). Average monthly discharge was strongly related to total monthly rainfall in winter (R^2 = 0.64, $p<0.001$, Fig. 4.2d)). In summer this relationship was less pronounced but still significant (R^2=0.39, p=0.003, Fig. 4.2d). The same increase in rainfall results in bigger discharge differences in winter than in summer. Discharge data from Antwerp show a similar pattern.

4.3.2 Nutrient concentrations and fluxes

In general, concentrations decreased at Dendermonde and Antwerp as water discharged increased, and this decrease was mainly apparent in winter (Table 4.1). Average winter concentrations in 1999-2000 (average of all winter period observations in period 1999-2000, period with high discharges) of ammonia and totP were only half the concentrations observed in 1996-1997 (period with lower discharges). TDIN, totN and DRP concentrations decreased by around 20-30%. In summer (average of all summer observations in periods 1996-1997 vs. 1999-2000), concentrations did not drop likewise. In Antwerp, totN and TDIN even increased. A Wilcoxon Rank-Sum test was

performed to test the significance of the observed differences (Table 4.1). In contrast to other nutrients, nitrate concentrations increased by around 20 % in Antwerp in winter

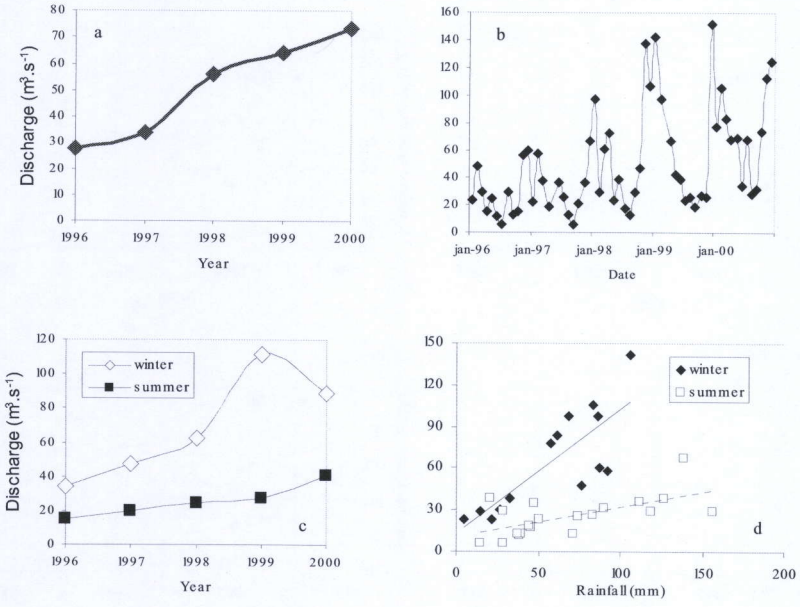


Fig. 4.2: Discharge at Dendermonde 1996-2000 (source: AWZ); a) Yearly averaged discharge; b) Seasonal patterns; c) Yearly winter and summer averages; d) Discharge dependence (least-squares regression) on rainfall. Monthly averaged discharged at Dendermonde versus total monthly rainfall at Geraardsbergen (source: KMI, Royal Meteorological Institute) (Least-squares regression: summer p=0.003, R^2=0.39, F=12; winter p=0.0006, R^2=0.64, F=22).

and summer and in Dendermonde in winter. Summer nitrate concentrations in Dendermonde slightly decreased, while oxygen conditions tripled in the freshwater zone. However, this improvement was not observed farther downstream. Winter concentrations of dissolved silica (DSi) remained virtually constant, but summer concentrations greatly increased over the 5-year study period, especially in Antwerp. Water quality over the studied period in the Rupel showed similar patterns as in Antwerp. No Wilcoxon-test was performed for the Rupel for winter data, due to less frequent data in the 1996-1997 period. In contrast to the other sites, at Vlissingen nitrate, silica, DRP and TDIN concentrations greatly increased, while totP

concentrations were stable (Table 4.1, Fig. 4.3). No yearly average is shown for 1996, because in winter there was no sampling at Vlissingen.

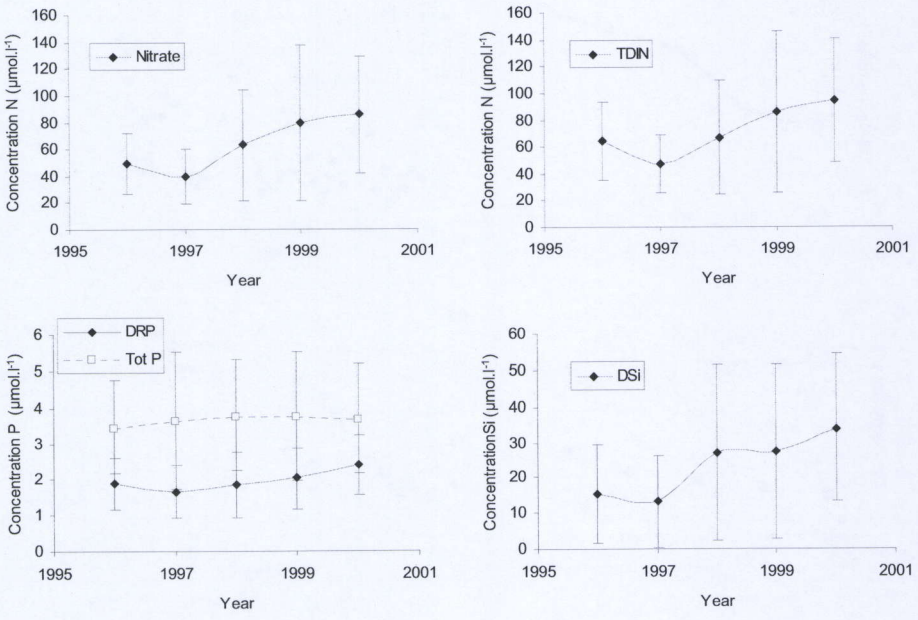


Fig. 4.3: Yearly averaged TotP, DRP-, DSi-, NO_3^-- and TDIN concentrations at Vlissingen (1997-2000), DRP = dissolved reactive phosphorous, TDIN = total dissolved inorganic nitrogen

In contrast to nutrient concentrations, discharged loads of nutrients generally increased throughout the study period. Total discharged loads of DRP, totP (Fig. 4.4a), nitrate, TDIN (Fig. 4.4b), dissolved silica (Fig. 4.4c) and chloride (Fig. 4.4d) showed clear increasing trends over the study period in the freshwater zone. Ammonia loads remained more or less constant (Fig. 4.4b). The relative proportion of nitrate in the total nitrogen load increased steadily. Similar results were observed at Antwerp and in the Rupel (not shown). However, totP loads did not increase in Antwerp. TotP loadings here were lower than the sum of Rupel and upstream freshwater totP loads. In the Rupel, totP loads only increased in 2000. At Vlissingen, total discharged load of totP, DRP (Fig. 4.4e), TDIN and nitrate (Fig. 4.4f) showed no real consistent trend. Discharged loads of silica nearly doubled (Fig. 4.4g). Ammonia loads dropped to near

zero over the same period (Fig. 4.4e). Discharged nitrogen, silica and phosphorus loads were much higher at Vlissingen than upstream at Dendermonde.

Table 4.1: Average winter- and summer concentrations (all µmol L^{-1}, except oxygen) of oxygen (mg L^{-1}), nitrate, ammonia, TDIN, totN, DRP, totP and Si at Dendermonde, Antwerp, Vlissingen and in the Rupel. Comparison for the periods 1996-1997 and 1999-2000 and procentual difference. [ ] = concentration, n = number of measurements, p = significance value of Wilcoxon Rank Sum test. Bold = significant difference (p<0.05) between period 1996 for this parameter

	summer						winter					
parameter	summer 96-97		summer 99-00				winter 96-97		winter 99-00			
Dendermonde	[]	n	[]	n	%	p	[]	n	[]	n	%	p
O_2 (mg.l^{-1})	**0,35**	**8**	**1,57**	**8**	**349**	**0,02**	**5,41**	**5**	**6,87**	**5**	**27**	**0,03**
NO_3^-	306	8	292	8	-5	0,40	346	5	445	5	28	**<0,01**
NH_4^+	154	8	127	8	-18	0,64	422	5	154	5	-64	**<0,01**
TDIN	492	8	443	8	-10	0,21	781	5	611	5	-22	**<0,01**
totN	651	8	569	8	-13	0,09	902	5	694	5	-23	**<0,01**
DRP	23	8	20	8	-14	0,29	21	5	12	5	-42	**<0,01**
totP	47	8	34	8	-28	0,05	43	5	21	5	-52	**<0,01**
Si	94	7	131	8	39	0,42	223	2	233	5	4	**
Antwerp												
O_2 (mg.l^{-1})	1,24	8	1,01	8	-19	0,49	4,12	6	5,59	6	36	0,11
NO_3^-	241	8	286	8	19	0,10	291	6	356	6	22	0,11
NH_4^+	74	8	53	8	-29	0,67	368	6	149	6	-60	**<0,01**
TDIN	329	8	359	8	9	0,12	662	6	513	6	-23	**<0,01**
totN	429	8	443	8	3	0,49	733	6	569	6	-22	**<0,01**
DRP	9	8	8	8	-11	0,37	8	6	5	6	-35	**0,02**
totP	17	8	14	8	-21	0,06	18	6	9	6	-50	**<0,01**
Si	**50**	**7**	**121**	**8**	**140**	**0,04**	222	3	221	6	-1	**
Rupel												
O_2 (mg.l^{-1})	1,04	8	1,05	8	1	0,83	2,03	2	5,09	6	151	**
NO_3^-	131	8	154	8	17	0,83	221	2	266	6	20	**
NH_4^+	244	8	206	8	-16	0,49	375	2	169	6	-55	**
TDIN	395	8	389	8	-2	0,83	607	2	445	6	-27	**
totN	527	8	510	8	-3	0,60	671	2	506	6	-25	**
DRP	14	8	11	8	-23	0,14	8	2	6	6	-26	**
totP	34	8	21	8	-37	0,14	18	2	9	6	-51	**
Si	**125**	**7**	**203**	**8**	**63**	**0,02**	234	2	233	6	0	**
Vlissingen												
O_2 (mg.l^{-1})	7,62	8	7,16	8	-6	0,40	10,36	3	9,67	6	-7	**
NO_3^-	30	8	47	8	57	0,06	68	3	139	6	104	**
NH_4^+	7,5	8	5,3	8	-29	0,92	22	3	8	6	-64	**
TDIN	39	8	54	8	38	0,07	92	3	150	6	63	**
totN	**	**	**	**	**	**	**	**	**	**	**	**
DRP	1,7	8	1,9	8	12	0,46	1,8	3	2,8	6	56	**
totP	2,9	8	2,9	8	0	0,83	4,7	3	4,5	6	-4	**
Si	**5,1**	**8**	**10**	**8**	**96**	**0,02**	36	3	57	6	58	**

4.3.3 Discharge dependence of concentrations

Discharge was an important causal factor in observed nutrient concentration variability throughout our study period. In winter, oxygen-, TDIN-, totN-, totP- and ammonia-concentrations were linearly dependent on discharge in Dendermonde, Antwerp and the Rupel (Table 4.2). For oxygen, this relationship was positive; the other variables were

negatively related to discharge. DRP was negatively related to discharge in Dendermonde and Antwerp, but not in the Rupel. Dissolved silica was totally independent of discharge in winter. For totN, TDIN, ammonia and DRP, linear relationships were not observed in summer, in contrast to winter (Table 4.2). Dissolved silica was positively linearly dependent of freshwater discharge at Antwerp and Dendermonde in summer (Table 4.2).

Table 4.2: Discharge dependence (total monthly discharges) of monthly concentrations of oxygen, nitrate, ammonia, TDIN, totN, DRP, totP and Si at Dendermonde, Antwerp and in the Rupel for winter (up) and summer (down) (least-squares linear regression, data were log-transformed for normalization). +/- indicates a positive respectively a negative relation, bold underlined=significant relationship ($p<0.05$)

winter												
	Rupel				Dendermonde				Antwerp			
parameter	p	+/-	R^2	F	p	+/-	R^2	F	p	+/-	R^2	F
O_2	**0,007**	+	**0,57**	**12**	**0,005**	+	**0,56**	**13**	**0,007**	+	0,50	11
NO_3^-	0,056	+	0,35	5	**0,005**	+	**0,53**	**12**	0,480	+	0,04	1
NH_4^+	**0,008**	-	**0,56**	**12**	**0,001**	-	**0,61**	**17**	**0,020**	-	**0,37**	**7**
TDIN	**0,032**	-	**0,42**	**6**	**0,029**	-	**0,36**	**6**	**0,002**	-	**0,57**	**16**
totN	**0,004**	-	**0,63**	**15**	**0,001**	-	**0,62**	**18**	**0,001**	-	**0,63**	**21**
DRP	0,101	-	0,27	3	**0,006**	-	**0,51**	**12**	**0,030**	-	**0,34**	**6**
totP	**0,002**	-	**0,66**	**18**	**0,002**	-	**0,62**	**18**	**0,021**	-	**0,37**	**7**
Si	0,096	-	0,28	4	0,630	-	0,03	0	0,570	-	0,03	0

summer												
	Rupel				Dendermonde				Antwerp			
parameter	p	+/-	R^2	F	p	+/-	R^2	F	p	+/-	R^2	F
O_2	**0,017**	+	**0,28**	**7**	0,070	+	0,18	4	0,510	-	0,02	1
NO_3^-	0,053	+	0,19	4	**0,023**	-	**0,26**	**6**	0,950	+	0	0
NH_4^+	0,17	-	0,10	2	0,053	+	0,19	4	0,160	+	0,11	2
TDIN	0,62	-	0,01	0	0,620	+	0,01	0	0,230	+	0,08	2
totN	0,54	-	0,02	0	0,410	-	0,04	1	0,290	+	0,06	1
DRP	0,16	-	0,11	2	0,600	-	0,02	0	0,910	-	0,08	0
totP	0,22	-	0,08	2	0,270	-	0,07	1	0,920	-	0,01	0
Si	0,57	+	0,02	0	**0,006**	+	**0,37**	**10**	**0,019**	+	**0,28**	**7**

The relation between discharge and DSi-, ammonia- and nitrate- concentrations in the tidal freshwater was further studied in the periods October-March (low biological activity) and April-September (high biological activity) (Fig. 4.5). The distinction between low and high biological activity in the chosen periods was ecologically relevant. The repective periods showed low and high chlorophyll-a concentrations respectively throughout the estuary (Van Damme *et al.*, 2005) DSi-, ammonia- and nitrate-concentrations showed opposite relations with discharge over the five-year study

period in the respective periods. Chloride shows the same relationship with discharge in both periods: higher discharges lead to lower chloride concentrations in the freshwater.

4.4 Discussion

4.4.1 Fluxes in the freshwater and brackish zone

Based on a compilation of the scattered data of water quality of the Schelde estuary in the period 1965-1995, Van Damme *et al.* (1995) showed that water quality was worst during the 1970's when large parts of the brackish and fresh part of the estuary were anoxic. Investments in both industrial and urban wastewater treatment reduced organic loadings which resulted in increasing oxygen conditions since 1980 from ca. 3 mg L^{-1} to 5 mg L^{-1} in 1995 (year averaged values) near the Dutch-Belgian boarder. At the same sampling point, ammonia-concentrations decreased since 1980 from ca. 214 µmol L^{-1} to 71 µmol L^{-1}, while nitrate-concentrations increased (ca. 214 µmol L^{-1} to 357 µmol L^{-1}). DRP-concentrations clearly decreased since the early 1980's from ca. 20 µmol L^{-1} to 7 µmol L^{-1}.

A further improvement of the water quality, based on concentrations, between 1996 and 2000, is clear in winter, both in the freshwater and brackish zone. TDIN-, totN-, DRP- and NH_4^+-concentrations dropped, while oxygen-concentrations rose. Discharge seems an important causal factor in the latest concentration drops. Dilution in higher water volumes has been observed to have a positive impact on nutrient and pollutant concentrations in the upper Clyde estuary and the river Wear (Scotland) (Curran & Robertson, 1991; Neal *et al.*, 2000).

The hypothesis of dilution with higher freshwater discharges and rainfall could be further supported by the chloride dilution patterns with higher discharge. Freshwater bodies receiving chloride mainly from precipitation differ, according to Gibbs (1970), from freshwater bodies receiving chloride from soil erosion. The difference is made according to total salt concentration and the ratio of Cl to the sum of Cl and HCO_3. With an average chloride concentration of 83 ppm (5 year average 1996-2000, Schelde river upstream Gent, beyond tidal influence) the chloride supply to the freshwater Schelde would, according to this division, not be rainwater dominated but erosion dominated. Non-point sources could probably include both run-off from industry and

agriculture in the upstream region and run-off from roads treated against snow and ice as well as soil erosion. Rainfall dilutes chloride concentration in freshwater bodies receiving chloride mainly from erosion, as was observed over the study period.

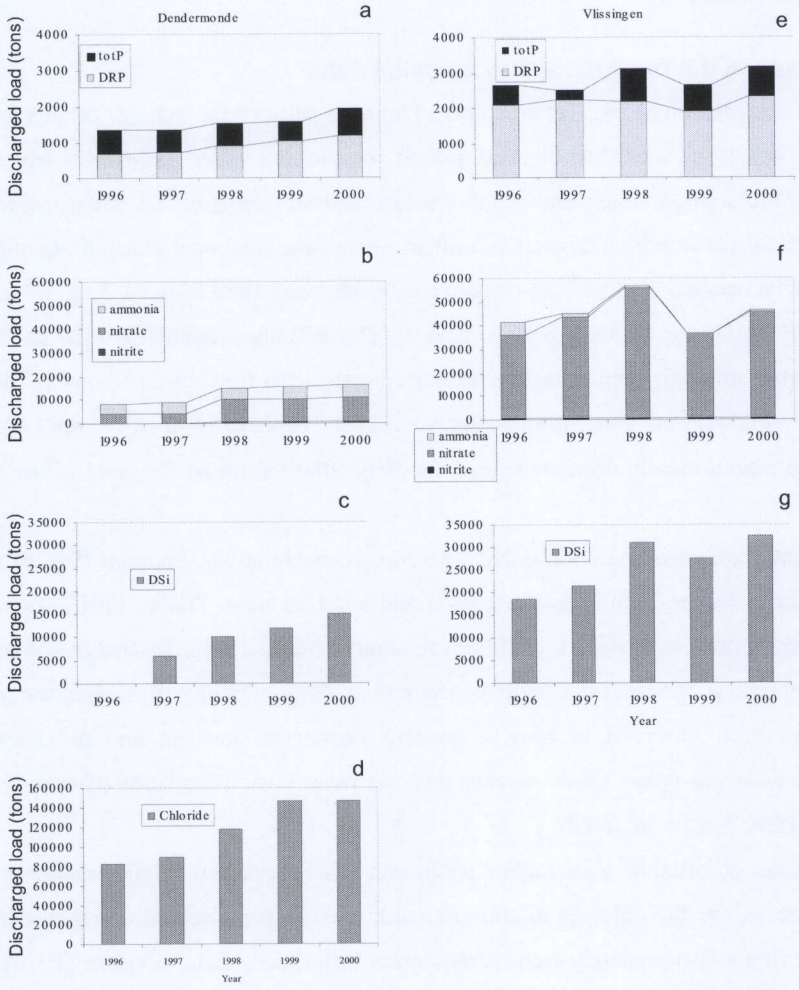


Fig. 4.4: Yearly total discharged loads at Dendermonde (a-d) and Vlissingen (e-f): a),e) DRP and totP; b),f) TDIN, nitrate, ammonia, nitrite; c),g) silica; d) chloride

The strongest indication for increasing non-point surface run-off input is the observation that, along with increased discharges, an increased load of eroded material is imported

to the Schelde estuary (Fig. 4.6). Over 50 % of this suspended matter originates from land erosion (source: AWZ). Higher rainfall induces a higher diffuse input of materials to the estuary.

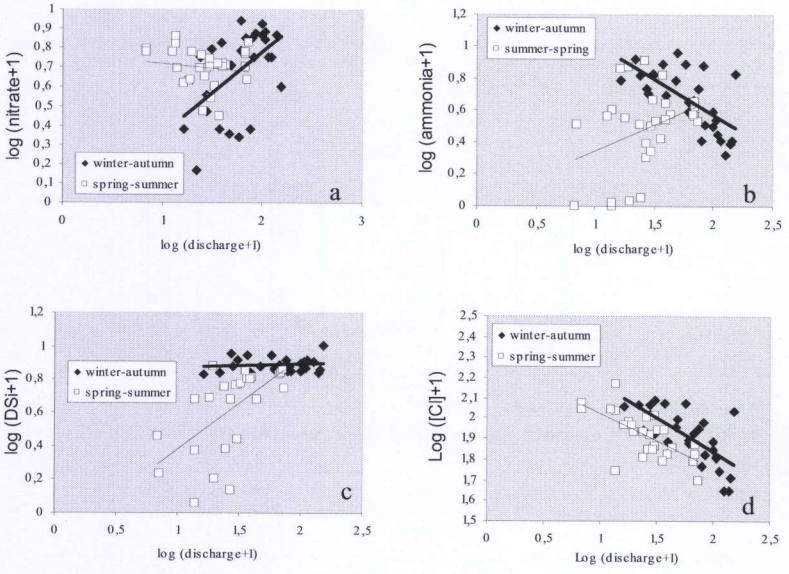


Fig. 4.5: Relation (least-squares linear regression) between total monthly discharge and monthly nutrient concentrations in spring-summer (April-September) and autumn-winter (October-March) at Dendermonde. a) nitrate (summer-spring p=0.40, R^2=0.03; winter-autumn p=0.003, R^2=0.29) b) ammonia (summer-spring p=0.06, R^2 = 0.13, winter-autumn p=0.0001, R^2=0.44) c) silica (summer-spring p=0.0007, R^2=0.39, winter-autumn p=0.53, R^2=0.02) d) chloride (summer-spring p=0.00003, R^2=0.47, winter-autumn p=0.00002, R^2=0.51)

Increased surface run-off of sediments induced increasing non-point input of nutrients. Nutrient loss from agricultural lands by rainfall land erosion can be estimated from knowledge of soil loss (Hargrave & Shaykewich, 1997). Higher inputs of nutrients to the estuary from diffuse sources explain the strong increase of nutrient loadings in the upper estuary. Increasing nitrogen discharges at Antwerp and agriculture N-loss (as calculated by VMM, Flemish Environmental Agency) from agricultural soil over Flanders show similar patterns (Fig. 4.7). The absence of increased loadings for ammonia, with little diffuse input origins, in winter, supports the origin from diffuse input sources. The change in relative proportion of ammonia and nitrate can be

explained by rising oxygen concentrations with higher discharges, resulting in more intense nitrification and a decrease in denitrification, an anaerobic process (Seitzinger, 1988; Billen & Garnier, 1997).

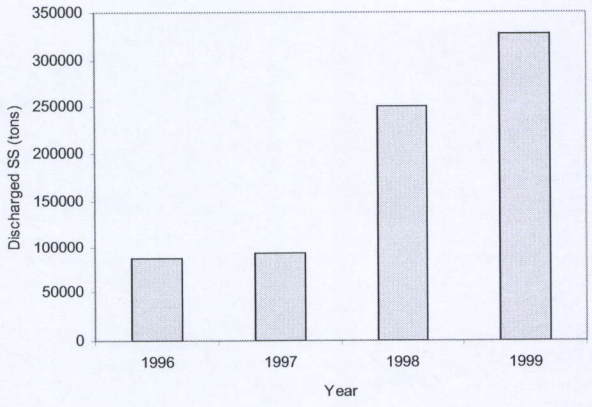


Fig. 4.6: Total discharged suspended solids (SS) by the Schelde (downstream Rupel). Yearly totals. (Taverniers 1999)

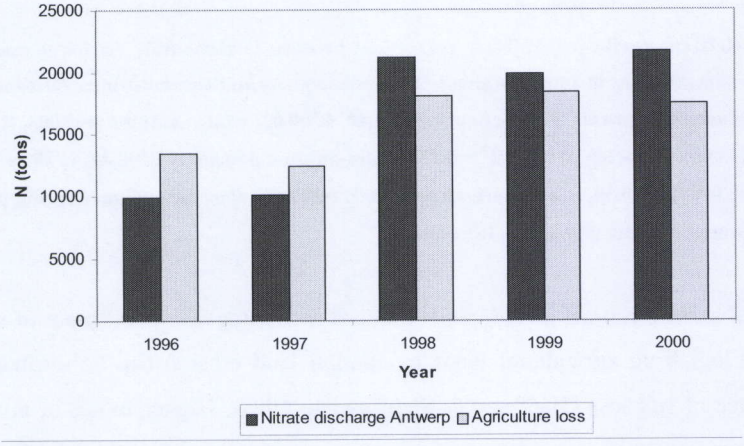


Fig. 4.7: Yearly total discharged nitrate loads at Antwerp vs. total yearly estimated agriculture loss of nitrogen in Flanders Schelde Basin (source VMM, Flemish Environmental Agency, Model Sentwa 4.06)

The increasing discharges of total P in the freshwater estuary apparently do not result in increasing discharges farther downstream in the brackish zone. This could be explained

by retention and sedimentation of P within the turbidity maximum, at the freshwater-saltwater interface (Wollast, 1982; Zwolsman, 1994). This could also explain the less clear trend of totP in the Rupel, situated near the turbidity maximum. This hypothesis is supported by the observation that totP loadings at Antwerp are lower than the sum of Rupel and freshwater estuarine loadings.

The impact of respiration and nitrification, processes that increase in efficiency with higher temperatures, on the organic matter and nitrate load, was lowered due to lowered residence times in the freshwater, and less oxygen was used. In summer, high oxygen conditions only occurred at peak-discharges in the freshwater zone. Higher loads of ammonium and organic material were transferred to the downstream regions (Antwerp) due to lower residence times and further processed in the brackish zone by respiration and nitrification, which causes oxygen conditions to remain very low downstream of the freshwater zone. The prolongation of the ammonium removal distance with higher discharges was observed earlier in the Alaska tundra (Vörösmarty & Peterson, 2000). The significant negative relation between discharge and nitrate concentrations (less ammonia is nitrified to nitrate at high discharges) in summer and spring in the fresh water supports this hypothesis. In winter on the other hand, when nitrification and respiration are less intense than in summer, oxygen concentrations increase concurrently with increasing discharge. As a result, nitrification was enhanced in winter at higher discharges. Balls *et al.* (1996) observed a comparable relation between oxygen and discharge in the Forth estuary. All these effects of increasing discharge on ammonia and nitrate concentrations in the periods April-September (higher temperature, nitrification more efficient) and October-March (low temperature, nitrification less efficient) in the freshwater in the end resulted in decreasing seasonal concentration variability. The secondary effects of increasing discharge on nutrient concentrations through increasing oxygen concentration, can add to observed dilution effects. Higher oxygen conditions result in less DRP due to binding reactions with suspended matter (Krom & Berner, 1980; Froelich, 1988).

The biogeochemistry of dissolved silica (DSi) is totally different from that of other nutrients. Silica plays an important role in coastal eutrophication problems (Schelske *et al.*, 1983; Lancelot *et al.*, 1987; Smayda, 1990; Smayda, 1997). In contrast to other nutrients, no important anthropogenic input of silica exists. Dissolved silica (DSi)

originates from biogeochemical reactions which set free dissolved silica from alkali and aluminum silicate minerals (Hutchinson, 1957; Correll *et al.*, 2000). In the period October-March, silica concentration is totally independent of discharge conditions. Seasonal variability in DSi is caused by uptake by diatom communities in spring and summer, which results in lower DSi-concentrations. However, with highest discharge conditions, summer and spring concentrations equal winter concentrations in the freshwater Schelde estuary. Freshwater diatom blooms are negatively influenced by higher discharge conditions, and complete diatom communities are "flushed" away by peak discharges. Extreme runoff events were already shown to cause flushing of the entire freshwater reach, whereby the estuarine phytoplankton community is replaced with one of riverine origin, not adapted to growth conditions within the tidal area (Muylaert *et al.*, 2001). With the flushing of plankton, no DSi uptake takes place, which causes summer-spring concentrations to approach winter-autumn concentrations. In parallel with the influence of discharge on nitrate and ammonia concentrations, rising discharge conditions result in the diminution of seasonal differences in silica concentrations. Farther downstream, in Antwerp and at the Rupel, these effects are still manifest. At Antwerp, silica concentrations have more than doubled over the study period.

4.4.2 Fluxes to the coastal zone

Increasing water discharges have multiple effects on the nutrient status of coastal waters near Vlissingen. With higher discharges, the estuarine plume expands farther into the coastal waters. As a result, salinity has decreased at Vlissingen over the five-year study period (Fig. 4.8). Due to conservative mixing with seawater, nutrient concentrations in the Westerschelde decrease when moving towards saltier water (Ouboter *et al.*, 1998). This explains the rising concentrations of Si, DRP, NO_3 and TDIN near Vlissingen from 1996 to 2000.

Discharged silica loads at the mouth of the estuary have increased along with increasing silica discharges at Antwerp and Dendermonde. This load could have further increased due to decreasing salinity and increasing suspended matter in the Westerschelde, which could both have reduced diatom growth in the Westerschelde.

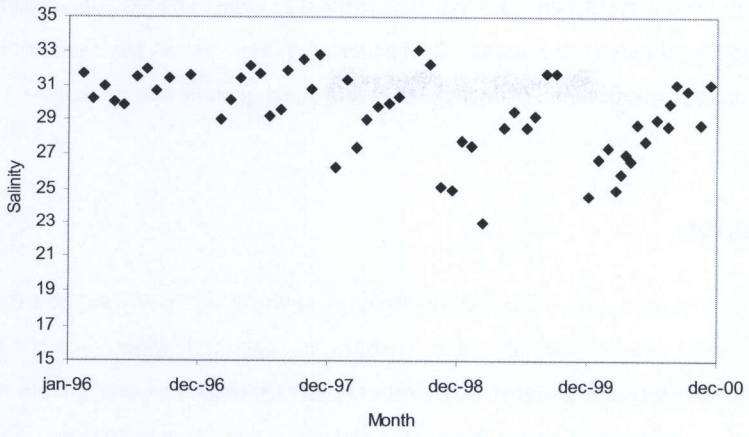


Fig. 4.8: Monthly salinity at Vlissingen (1996-2000)

In contrast to DSi loads near the mouth and nitrate, totP and DRP loads upstream, nitrate, totP and DRP discharges did not increase at Vlissingen. As mentioned earlier, P-retention occurs in the high turbidity zone, which could explain the absence of any trend in total P discharges downstream the turbidity maximum. The absence of any trend in NO_3-discharge to the North Sea, despite massive increases upstream, is not so readily explained and a challenge for future research. Furthermore, nitrate-, TDIN-, DRP-, totP- and silica discharges are much higher near the mouth of the estuary than at Antwerp. A big part of these increased loadings probably results from the influx from the channel Gent-Terneuzen (which flows into the estuary near Terneuzen, Fig. 4.1) and other lateral inputs of nutrients and the degradation of organic matter, flushed through by higher discharges.

Similar results and predictions for the pivotal role climate and hydrology can play in determining the nutrient fluxes to coastal ecosystems have been obtained in other systems across the world. The balance between storage of nitrate in the terrestrial ecosystem and leaching of the nitrate was recently shown to be dependent on hydrology and climate in a long-term study in the Mississippi-basin (Donner *et al.*, 2002). In the Hudson estuary (USA), effects of residence times on primary production have been reported (Howarth *et al.*, 2000). During periods of low freshwater discharge, a combination of longer residence time and deepening of the photic zone, led to increasing susceptibility of this system to eutrophication. Scavia *et al.* (2002)

summarised the potential effects of climate variability and change on coastal ecosystems and highlighted increasing freshwater delivery as a key factor in determining estuarine stratification, residence times and consequently eutrophication.

4.5 Conclusion

The effects of flow variation on estuarine functioning shown in this study suggest that global change could induce several major changes in estuarine water quality. In freshwater and brackish reaches, higher discharges apparently improve water quality by diluting nutrient concentrations and a positive effect on oxygen concentrations. This masks a problem of increasing total loadings of nutrients. The effect of increasing discharge on ammonia, nitrate and Si-concentrations is opposite in spring and summer than in autumn and winter. Future global change could flatten out the seasonal cycles for these nutrients. Although increasing loads observed upstream were not unambiguously visible near the mouth of the estuary in this study, it is clear that higher discharges of nutrients in the upper estuary, caused by increasing non-point input, could pose a major problem to governments trying to reduce nutrient inputs to estuarine coastal regions. For example, in the 1990s, the Flemish government strongly increased efforts to reduce waste input to the brackish and fresh area (Fig. 4.9). These efforts have mainly concentrated on point sources of nutrient pollution. The vast amounts of money invested in point-pollution reduction did not result in decreasing total discharges of N to coastal waters, due to the changing hydrological conditions. In contrast, total N-discharges even increased. In the Seine estuary (France) and the Schelde, it was predicted that reduced organic C input to estuaries would result in increasing discharges of N to coastal waters due to a decrease in denitrification (Soetaert & Herman, 1995; Billen & Garnier, 1997). Increasing freshwater discharge and surface run-off will only add to this problem. The importance of reducing non-point nutrient input to the estuary concurrently with the reduction of point-pollution, was clearly pointed out in Chesapeake Bay (USA) (Boesch *et al.*, 2001).

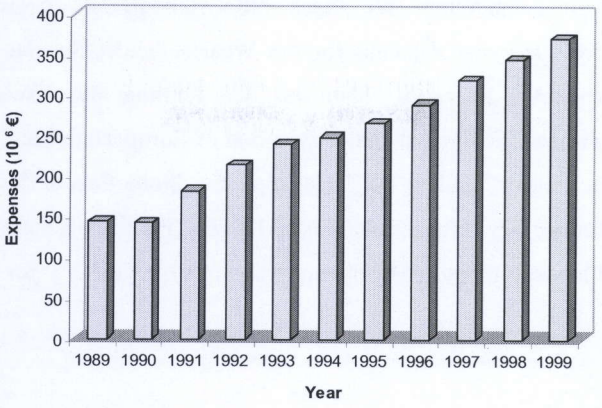


Fig. 4.9: Expenses made by Flemish governmental institutes to reduce point source pollution to surface waters (1996-2000) Source: VMM, Flemish Environmental Society

In this context of global change, measures to reduce diffuse inputs from mainly agricultural sources are more urgent than ever. The European directive on the control of nitrates requires the creation of nitrate-vulnerable zones. In these zones, both wetland restoration and changes in agricultural practices must be implemented (Ducrotoy *et al.*, 2000). Riparian vegetation can significantly reduce non-point nutrient flows to surface waters (Lowrance *et al.*, 1985; Correll *et al.*, 1992). Furthermore, creating more wetlands and thus giving more space to the water, could result in higher water residence times. This could prove to be the solution to the problem of the flushing of entire diatom communities from estuarine freshwater reaches and reduce the flattening out of seasonal cycles.

Acknowledgements

Zeeschelde samples were analysed in the "UA, University of Antwerp, Department of Biology, Testing Laboratory for Chemical Water Quality" by Lieve Clement and Eva De Bruyn. Samples were taken from the "MS Veremans" (AWZ, division maritime Schelde) and the "Scaldis I" (AWZ, division Zeeschelde). We would like to thank Lieve and Eva and all the crew of the sampling ships. We would also like to thank VMM and the financers of the OMES (Research Environmental Effects Sigmaplan)-monitoring-

project for their cooperation. We thank NIOO-CEME (Peter Herman and Jack Middelburg) for supplying the data for the Westerschelde. Special thanks to FWO (Fund for Scientific Research, Flanders) for funding the "Scientific Research Community" project "Ecological characterization of European estuaries, with emphasis on the Scheldt estuary" and to IWT (Institute for Promotion of Innovation through Science and Technology, Flanders) and NWO-FWO (Fund for Scientific research, The Netherlands, Flanders, Flemish-Dutch cooperation "VLANEZO") for scientific project funding.

Chapter 5

Measured denitrification and nitrous oxide fluxes in intertidal mudflats along the Zeeschelde (Scheldt estuary, Belgium)

Van Damme S., Starink M., Van der Nat J., Struyf E., Van Cleemput O. & Meire P.

Abstract

Seasonal measurements were carried out of denitrification, using the acetylene inhibition method on laboratory incubated sediment samples, concurrent nitrate consumption rates, and N_2O emission measurements in field and laboratory conditions along a longitudinal and vertical gradient of mudflats in the Scheldt estuary, Belgium. Additional experiments were carried out to determine limitation of nitrate vs. carbon, oxygen consumption and to investigate the role of flooding regime on N_2O emission. Spatial and temporal variation of the gaseous emissions was high and correlation with ambient parameters was generally not significant. Laboratory incubated denitrification values ranged from 0.22 to 6.8 mmol N m^{-2} d^{-1}, concurrent N_2O emissions ranged from 0.005 to 0.48 mmol N m^{-2} d^{-1} and field incubated N_2O emissions at low tide ranged from 0 to 0.49 mmol N m^{-2} d^{-1}. Although nitrate was limiting for denitrification, N_2O emission at 10kPa acetylene incubation and constant nitrate availability decreased with rising tide. Oxygen consumption related with the presence of macrozoobenthos (*Oligochaeta*) was with 1.23 mol O^2 mol C^{-1} d^{-1} higher than previously assumed. It is hypothesised that benthos affects denitrification not only by enhancing nitrate transport from the overlying water into the sediment, but also by reducing the oxygen concentration at the water sediment interface.

5.1 Introduction

Among the numerous goods and services provided by estuaries, nutrient cycling is often prominent. In one case (Shepherd *et al.*, 2007), nitrogen cycling amounted up to nearly the complete estuarine habitat value as given by Costanza *et al.* (1997). Denitrification is the main process that accounts for the ecosystem services of the nitrogen cycle, although it is directly linked with emission of trace gas involved in global warming and stratospheric ozone destruction (Seitzinger *et al.*, 1984; 1988). In many studies on N-cycling in estuarine habitat, denitrification is determined in different indirect ways: as a rest fraction in mass balances (*e.g.* Middelburg *et al.*, 1995a; Van Damme *et al.*, 2009) or isotope budgets (*e.g.* Gribsholt *et al.*, 2005), or through modeling (*e.g.* Soetaert *et al.*, 1995; Vanderborght *et al.*, 2002). Direct measurements of estuarine denitrification, with the acetylene inhibition technique, microsensors, direct measurement of N_2 emission in a He background or isotope measurements of nitrogen gas are less common. For instance, several ecological models, including benthic and pelagic denitrification, are available of the Scheldt estuary (Soetaert *et al.*, 1995; Vanderborght *et al.*, 2002). In contrast, direct denitrification measurements are restricted to one study and one sampling station (Laverman *et al.*, 2007). Such measurements are more important than indirect determinations, as these could be more biased than previously thought. Indeed, in recent years our understanding of the estuarine nitrogen cycle has been amended with several new pathways, including anaerobic ammonium oxidation to N_2 (anammox). Annamox has a well documented importance in marine and coastal environments (Meyer *et al.*, 2005), but its role in estuarine N-cycling is still under investigation. Only a few estuaries have been examined so far, showing *e.g.* that N_2 production due to annamox ranged between 0 and 22% in the Chesapeake Bay (Rich *et al.*, 2008). Annamox could bias nitrification coupled denitrification estimates such as presented by Middelburg *et al.* (1995a). The acetylene inhibition technique, a well established method to measure denitrification (Seitzinger *et al.*, 1993), is unaffected by annamox as this process is almost completely inhibited at an acetylene concentration of 22 μM while effective denitrification inhibition to N_2O requires 4mM (Jensen *et al.*, 2007).

The role of benthic denitrification in the Scheldt is gaining relative importance on pelagic denitrification, as the ecological recovery of the estuary leads to higher oxygen concentrations in the pelagic environment(Cox *et al.*, submitted); the Scheldt estuary is but one of several systems in this situation (*e.g.* Billen *et al.*, 2005).

It is not the aim to assess the influence of new pathways on previous denitrification estimates, but to present data obtained by a reappraised method of a system that still lacks data. We report the first measured denitrification data of mudflat sediments of the Scheldt estuary that cover both the salinity gradient and a vertical gradient in the freshwater part, as measured with the acetylene inhibition technique. N_2O emission rates were recorded additionally. A comparison between the benefits of increasing benthic denitrification and the negative effect of N_2O emission is useful within the framework of ecosystem goods and services, as the greenhouse gas issue is of ever growing importance.

5.2 Material and methods

5.2.1 Study area

The Scheldt estuary is located in Northern Belgium (Flanders) and the Southwest Netherlands (Fig.1). It extends from the mouth at Vlissingen (km 0) till Gent (km 158); there tidal movement is stopped through a complex of sluices. The lower and middle estuary, the Westerschelde (55 km long), situated in the Netherlands, is a well mixed region characterized by a complex morphology with flood and ebb channels surrounding several large intertidal mud and sand flats. The surface area of the Westerschelde is 310 km^2, with the intertidal area accounting for 35% of the area. The Sea Scheldt, situated in Belgium, is single channeled and its surface amounts to only 44 km^2. The water quality of the Scheldt has been heavily impacted, especially in the Sea Scheldt (Van Damme *et al.*, 2005), but is now in a phase of partial recovery (Soetaert *et al.*, 2006). This study is confined to the Sea Scheldt (105 km long).

5.2.2 Sampling sites

Four intertidal mudflat sites were selected along the Sea Scheldt, largely on the basis of salinity and accessibility (Fig. 5.1). Groot Buitenschoor (GB) is situated in the brackish part, Burcht (BU) on the transition zone between the freshwater and the brackish zone, Durme (DU) and Appels (AP) in the freshwater part (Table 5.1). In Appels a lateral gradient of four stations was installed between low water level and the *Scirpus* spp. vegetation bordering the marsh (Table 5.1). Wooden boardwalks were constructed and used to reduce the disturbance caused by visits.

Campaigns were conducted on a monthly basis during 1996 (N_2O emission) and 1997 (N_2O emission and denitrification).

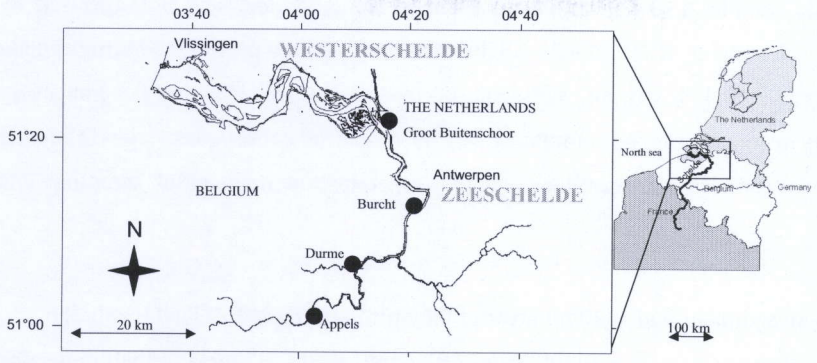


Fig. 5.1: Map of the selected sites

Table 5.1: Site description

Station	Elevation (m TAW)	Moisture (% DW)	Conductivity ($\mu S\ cm^{-1}$)	pH	C tot (% wt)	NH_4 (% wt)	$CaCO_3$ (% wt)	Sand (%)	Loam (%)	Clay (%)
GB	3.9	95 ± 13	15146 ± 9006	7.8 ± 0.3	3.0 ± 0.5	4.7 ± 4.3	17	30	46	25
BU	4.2	48 ± 19	2517 ± 1536	8.0 ± 0.1	1.2 ± 0.2	10.7 ± 5.0	12	60	29	11
DU	4.5	146 ± 22	1504 ± 319	7.8 ± 0.2	3.6 ± 0.8	19.3 ± 10.8	9.9	52	25	23
AP1	3.2	69 ± 20	1002 ± 362	7.5 ± 0.1	1.2 ± 0.6	10.9 ± 10.2	8.4	75	14	11
AP2	3.8	81 ± 22	1028 ± 281	7.5 ± 0.1	1.6 ± 0.2	10.6 ± 10.3	9.0	67	18	15
AP3	4.7	98 ± 30	1138 ± 206	7.3 ± 0.1	2.5 ± 0.8	8.7 ± 10.7	8.3	48	32	21
AP4	5.1	97 ± 37	1042 ± 344	7.5 ± 0.2	4.5 ± 1.2	3.5 ± 5.2	8.7	18	47	35

5.2.3 Field flux measurements

The release of nitrous oxide was measured by sampling accumulated gas beneath chambers placed over the sediment. Before placing them -about 4 cm deep in the sediment- the circular top lid was removed. This allowed chamber ventilation with ambient air while the sediment could re-establish equilibrium after the possible sediment disturbance due to placement of the chamber. The gas chambers had a circular ground surface of 176.7 cm^2, a height of 10cm and were made of non transparent polypropylene. The top lid contained a gastight septum at the top that was used for connection with Teflon vacutainers by means of a double needle, so that headspace samples could be transported and stored for analysis in the lab.

Samples were taken at t0 (*i.e.* immediately after closing the top lid) and half hour intervals during one hour (*i.e.* 3 in total per replicate).

5.2.4 Laboratory flux measurements

Sediment surface samples (~top 3 cm) were taken to the laboratory and homogenised by gentle stirring. Subsamples of 40 g fresh weight were then put into preweighed airtight glass recipients (volume 218.4 ± 0.8 ml, sediment horizontal surface 15.8 cm^2). For every sampling, fluxes were determined simultaneously in 6 sets of subsamples, with following treatments at two controlled temperatures (field temperature at moment of sampling and 25°C):

- N_2O from sediment with a 40 ml layer of 0.66 mM (10 mg N L^{-1}) KNO_3 solution
- N_2O from sediment with a 40 ml layer of 0.66 mM KNO_3 solution and with injection of 10 kPa acetylene in the headspace
- Nitrate water-sediment flux from a 40 ml layer of 0.66 mM KNO_3 solution

As soon as the solution was added, benthic invertebrates emerged from the sediment and showed activity that persisted during the entire flux measurements. Nitrous oxide fluxes under laboratory conditions (3 replicates) were determined by taking samples at t0 and at 24h intervals during 2 days. At this time lag under steady state conditions, all fluxes, calculated by regression analysis from the recorded change of concentration over time in the headspace, were significant ($p < 0.05$). Acetylene (10 kPa) was injected into the headspace to block conversion of N_2O to N_2 during denitrification. Shortcomings of the technique were thus limited by applying the incubations on small sediment volumes (40 g), enhancing the penetration of the acetylene gas, and by providing long incubation times (3d). Nitrate and ammonium fluxes were determined by sampling the overlying water layer in the separate subsamples at four to eight regular time intervals in separate replicates of a two days covering time series.

5.2.5 N vs. C limitation experiment

To investigate whether N or C was a limiting factor for denitrification, nitrate flux and N_2O-emission, laboratory flux measurements using homogenised sediment (as described above) were conducted at four different concentrations of nitrate (0, 1, 5 and 10 mg N L^{-1} as KNO_3) at 25°C. This experiment was carried out twice for sediment op Appels 2, Burcht and Groot

Buitenschoor, and 3 times for Durme. For each of these stations one experiment was carried out with and without addition of 1% glucose in the overlying solution.

5.2.6 Oxygen consumption experiment

In the same setup as the laboratory flux measurements (at 25°C), oxygen consumption from the overlying water was measured with a 'WTW OXI 91' oxygen meter. This was done on sediments of Groot Buitenschoor (samplings of 10 and 20/09/1996), Burcht (11 and 19/09/1996), Durme (3 replicates on sampling of 11/01/1996 and 2 replicates on sampling of 16/03/1996), Appels 2 (10 and 18/09/1996) and Appels 3 (17/09/1996). Sediment of Appels 3, that contained almost no benthic macro-invertebrates, was amended with and without addition of 100 individual Oligochaetes, collected on a 250µ sieve, corresponding with a density of 63290 ind. m^{-2} which is representative for an average site in the oligohaline part of the estuary (Seys *et al.*, 1999).

Oxygen consumption was calculated by determining the slope between -10% and -90% of the total oxygen concentration decrease during the experiment, relative to the initial concentration.

5.2.7 Experimental tidal mudflat

A mixture of (1:4) garden soil and mudflat sediment (Burcht) was mixed and transferred to a container (l x w x h = 2.0 x 0.5 x 0.8 m). The container was placed in a temperature (18±0.5°C), humidity (70±7%) and CO_2 concentration (380±40 ppmv) controlled room. The sediment was allowed to settle for a period of 4 months. After this period sediment height was ~35 cm. Two polypropylene collars with an inner diameter of 21 cm were installed in the centre of the container to ascertain consistent placement of the gas collecting chambers and minimise disturbance during successive emission measurements (Van der Nat & Middelburg, 2000). The flux chambers were 80 cm high (volume 55.4 l). A 16 hours day period with a light intensity of ~0.4mmol photons $m^{-2}.s^{-1}$ at the sediment surface (about 1.6 m below lamps) was set, except during the measurements when light was continuously supplied to avoid interference of the light regime with N_2O emission. Two tidal regimes (6 hours low – 6 hours high tide, and 10 hours low – 2 hours high tide resp.) were installed, each one during one week of which three days were used for allowing the sediment to come into equilibrium with the imposed tidal regime. The tidal range was ~16 cm. A large basin (~500 l) was used as a

reservoir for the overlying water. The nitrate concentration of the overlying water was daily adjusted at 10 mg N L^{-1}.

5.2.8 Analysis

Gas samples were transferred from the vacutainers or laboratory recipients to the detection equipment by means of 'Hamilton-GASTIGHT®' syringes. N_2O was determined using a Chrompack® 437A gas chromatograph, equipped with a stainless steel Altech Chromosorb 102 column of 4.88 m length and 3.175 mm diameter and a ^{63}Ni electron capture detector, under the following conditions: injector temperature 90°C, oven temperature 90°C and detector temperature 300°C. Standard gas of 51.4 ppmv N_2O in helium was used for calibration over a range of 10 – 1000 µL injection volume. For high tide conditions the N_2O concentration of the water phase was taken into account according to Moraghan & Buresh (1977).Nitrate and ammonium in water were determined according to Bremner (1965a).
Total carbon of the sediment was determined on air dry sediment according the method of Walkley & Black (Allison, 1965). Nitrate and ammonium in sediment were determined according Bremner (1965a) on extraction of 40 g sediment, extracted during 1h with 30 ml 3N KCl. Total N was determined after Kjeldahl destruction according Bremner (1965b). Sediment temperature was measured with a sediment thermometer at 2 cm depth. Conductivity of the pore water was measured with a WTW LF 91' conductivity-meter. pH of the sediment was measured in a sediment suspension according to Verloo (1988) with a C 832 Consort. Sediment texture was determined with a Sedigraph 5100. The CaCO3 content of sediment was determined through titration with HCl.

Estimates for annual nitrous oxide emission rates were calculated for all sites by integration of the curves connecting averages of replicate measurements. Months without data were interpolated linearly. Q10 values were determined on pair wise incubations at field temperature and 25 °C, and determined only if this temperature difference was at least 10°C.

5.3 Results

5.3.1 Site characterisation

The annual average sediment conductivity, carbon and nitrogen contents are listed in Table 5.1. The ammonium content of the sediment was in the freshwater stations generally higher

than in the brackish stations of Burcht and Groot Buitenschoor. The vertical gradient in Appels was generally characterised by an increasing total carbon content, clay and loam fraction and moisture content in upward direction. Dissolved nitrate concentrations (data not shown) were an order of magnitude lower than ammonium concentrations.

5.3.2 N_2O-Emission rates

Emissions of nitrous oxide from intertidal sediments of the Schelde estuary, as sampled *in situ* at low tide, and those determined after addition of nitrate solutions in the laboratory were highly variable, both temporal and spatial (Fig. 5.2-5.3). Negative fluxes were not recorded; all fluxes were from the sediment into the atmosphere. Laboratory incubated denitrification ranged from 0.22 to 6.8 mmol N m^{-2} d^{-1} (Fig. 5.2), concurrent N_2O emissions ranged from 0.005 to 0.48 mmol N m^{-2} d^{-1} (Fig. 5.3a) and field incubated N_2O emissions at low tide ranged from 0 to 0.49 mmol N m^{-2} d^{-1} (Fig. 5.3b). N_2O emissions in the field and in the laboratory after addition of nitrate solution thus were situated within the same range. On average, when a 10 mg N L^{-1} nitrate solution was applied at field temperature, N_2O emission with addition of acetylene was on average 51 times higher (3 to 345 times) than without acetylene. These high values indicate that denitrification was effective under ample nitrate provision. Denitrification removed between 3 and 60% (average 21%) of the nitrate in the overlying water.

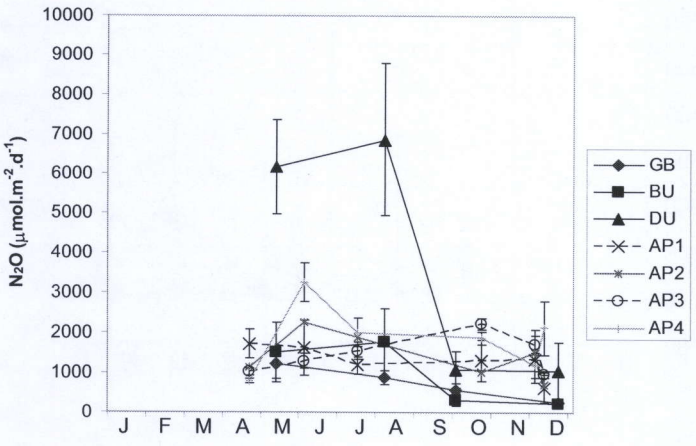


Fig. 5.2: Sediment denitrification; incubation in laboratory at field temperature, after addition of 10 mg N L^{-1} nitrate solution

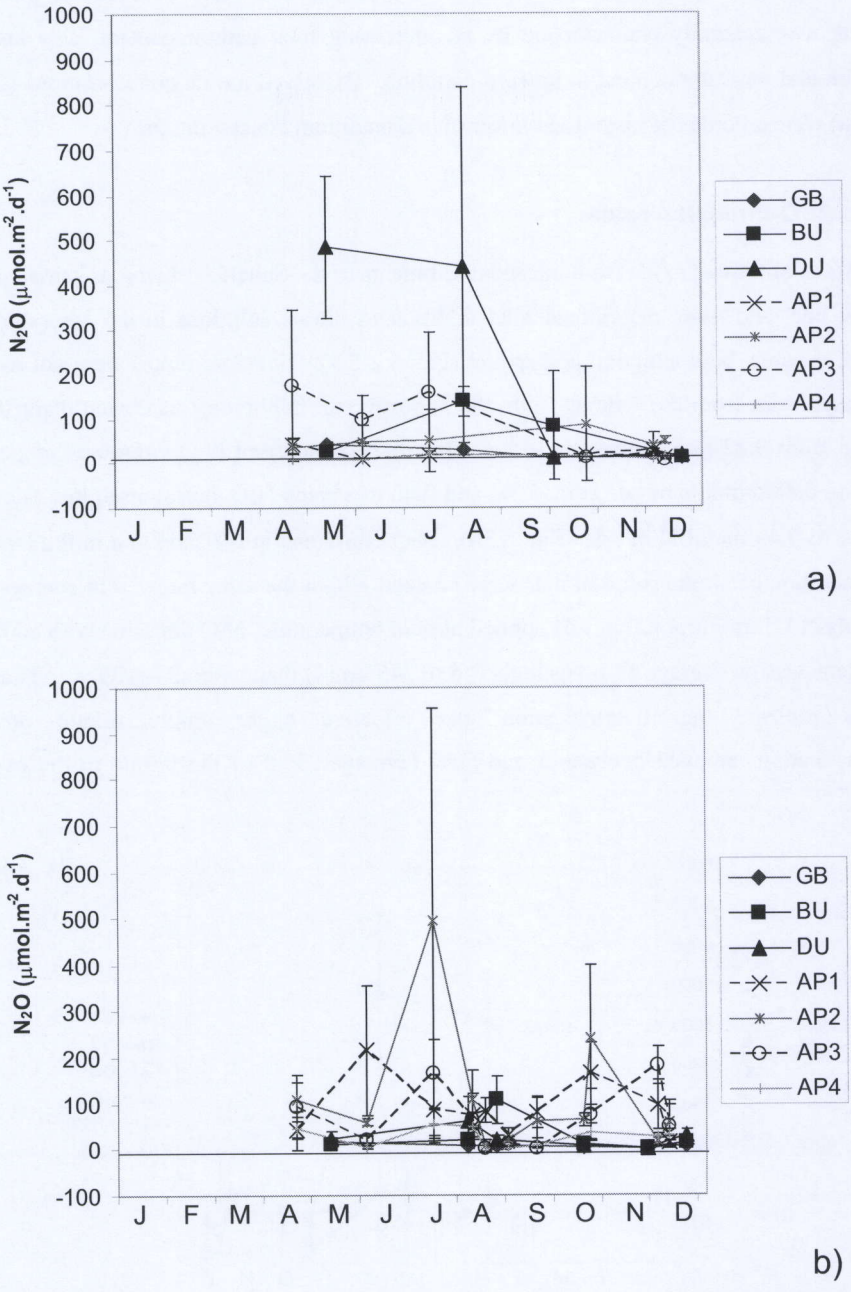


Fig. 3: N_2O emission from sediment; a) incubation in laboratory at field temperature, after addition of 10 mg N L^{-1} nitrate solution (data from 1996); b) *in situ* incubation at low tide (data from 1997)

In general, maximal values were recorded during summer and minima during winter (Fig. 5.2-5.3). Univariate analysis of variance on all replicates of the different sampling stations, with sampling month as a sorting variable, showed for denitrification significant variances ($p<0.05$) between sampling campaigns for all stations except Appels 1 and Appels 2 (Table 5.2). For Appels 3, however, the variance was related with a maximum denitrification value in winter (Fig. 5.2). In Appels, 3 of 4 stations thus showed no seasonality for denitrification. For laboratory incubated N_2O emissions, variances between sampling months were significant for all stations except for Burcht and Appels 2 (Table 5.2), but for Appels 1 and 4 the significant differences were very small. For field incubated N_2O emissions, not one variance between sampling months was significant. It can be concluded that the variance of the data was so large that seasonality was not clearly apparent.

Table 5.2: Univariate analysis of variance on all replicates of the different sampling stations, with sampling month as a sorting variable, for *in situ* and laboratory incubated N_2O emission and denitrification

Station	N_2O *in situ*			N_2O (10 mg NO_3^--N solution)			N_2O (10 mg NO_3^--N solution) (10 kPa acetylene)		
	df	F	p	df	F	p	df	F	p
GB	12	3.1	0.62	12	10.4	0,004	12	8.8	0,006
BU	12	2.2	0.12	12	2.6	0.12	12	5.9	0,02
DU	12	0.7	0.35	12	4.5	0,04	12	20.2	0,00
AP1	18	1.6	0.11	18	6.5	0,004	18	2.0	0.15
AP2	18	0.2	0.23	18	0.3	0.91	18	2.4	0.09
AP3	18	3.9	0.64	18	111	0,000	18	15.4	0,000
AP4	18	0.6	0.54	18	9.3	0,001	18	10.8	0,000

For laboratory incubated N_2O emissions (Fig. 5.4a) and denitrification (Fig. 5.4b), variability on the data was larger in the freshwater zone than at higher conductivity. This statement is, however, biased by the higher number of samples in the freshwater zone when taking also into account the data of the vertical gradient of Appels, as was done in Fig. 5.4. Univariate analysis of variance on data of only Durme, Burcht and Groot Buitenschoor, which are distributed more uniformly along the salinity gradient, showed, with specific conductivity as a sorting variable, a significant effect of specific conductivity between Durme and Burcht (denitrification: $F_{1,36} = 8.0$, $p = 0.001$; N_2O emission: $F_{1,36} = 25$, $p = 0.004$), but not between Burcht and Groot Buitenschoor.

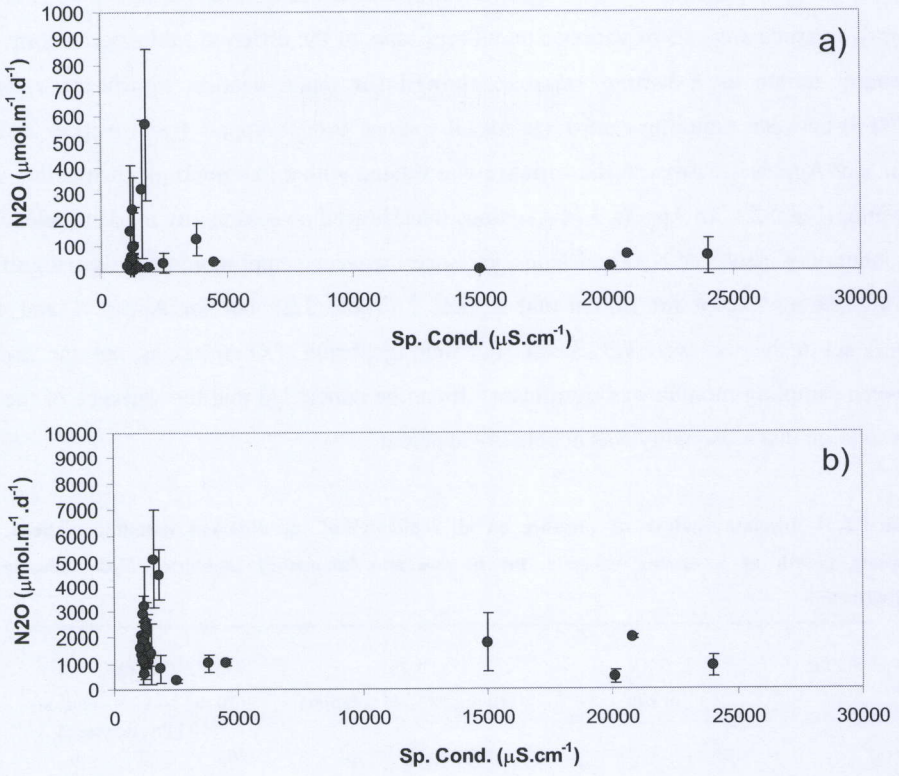


Fig. 5.4: Sediment N_2O emission (a) and denitrification (b) vs. specific conductivity of sediment interstitial water; incubation in laboratory at 25°C, after addition of 10 mg N L^{-1} nitrate solution

Univariate analysis of variance on all replicates, with location as a sorting variable, of the different sampling campaigns of the stations in Appels showed zero significant ($p<0.05$) differences for denitrification (data not shown). As such, for denitrification, no vertical gradient was observed at all.

For laboratory incubated N_2O emissions Appels 1 and Appels 4 showed both significantly lower values than both Appels 2 and Appels 3 (AP1-AP2: $F_{1,18}=6.3$, $p=0.018$; AP1-AP3: $F_{1,18}=35$, $p=0.009$; AP4-AP2: $F_{1,18}=2.3$, $p=0.002$; AP4-AP3: $F_{1,18}=42$, $p=0.012$). All other differences were not significant (data not shown).

For field incubated N_2O emissions, only one station showed consistently lower values. Appels 4 showed significantly lower values than all other stations (AP1: $F_{1,40}=45$, $p=0.008$; AP2: $F_{1,40}=12$, $p=0.013$; AP3: $F_{1,40}=1,8$, $p=0.024$). No other significant differences between stations were observed for field incubated N_2O emissions (data not shown).

Careful examination of the data revealed not a single factor, or any combination of measured variables, that could explain the temporal or spatial variation of the observed fluxes.

Estimates for annual nitrous oxide emission rates were calculated for all sites by integration under the curves that connect monthly averages of replicate measurements (Table 5.3). Months without data were interpolated linearly. Q10 values ranged between 0.7 and 2.6, showing thus high variability but within the range of biological processes.

Table 5.3: Annual integrated N_2O emission rates and Q_{10} values

Station	N_2O *in situ* (mmol $m^{-2} y^{-1}$)	N_2O (10 mg NO_3^--N solution) (mmol $m^{-2} y^{-1}$)	Q10	N_2O (10 mg NO_3^--N solution) (10 kPa acetylene) (mmol $m^{-2} y^{-1}$)	Q10
GB	3.6 ± 1.8	8.7 ± 4.7	1.5 ± 1.2	243 ± 122	2.0 ± 1.4
BU	7.7 ± 6.7	18 ± 15	0.9 ± 0.5	314 ± 232	1.0 ± 0.7
DU	8.9 ± 4.1	84 ± 76	1.2 ± 0.6	1335 ± 911	1.0 ± 0.4
AP1	29 ± 23	7.6 ± 3.4	2.6 ± 1.7	462 ± 116	1.3 ± 0.3
AP2	41 ± 48	19 ± 5.0	0.7 ± 0.3	472 ± 167	1.1 ± 0.5
AP3	26 ± 20	31 ± 21	1.0 ± 0.4	503 ± 154	1.3 ± 0.3
AP4	11 ± 5.5	4.3 ± 1.5	0.8 ± 0.3	538 ± 311	0.9 ± 0.3

5.3.3 N vs. C limitation experiment

As the nitrate concentration increased in the overlying solution (0, 1, 5 and 10 mg N L^{-1}), both the nitrate consumption rate and the denitrification rate increased (Fig. 5.5). Only in one case the increase was not significant (nitrate water-sediment flux Burcht, slope 0.02, R^2 0.01, $F_{1,8}$=8.2, p>0.5). Apart from this case the slope of nitrate water-sediment flux ranged from 0.32 to 2.14 (R^2 ranging from 0.78 to 0.99), and the slope of denitrification ranged from 0.09 to 0.98 (R^2 ranging from 0.82 to 0.99). Nitrate disappeared 2 to 5 times faster from the overlying solution than the according denitrification increase (Fig. 5.5). An additional similar experiment where the sediment was added in different recipients so that the water-sediment surface was 12.6 vs. 315 cm^2, *i.e.* 25 times larger, *ceteris paribus*, showed that the time before the overlying nitrate solution dropped from 10 to 2 mg N L^{-1}, was 4 days resp. 4 hours, *i.e.* 24 times shorter. The concordance between the surface increase and the nitrate consumption rate

decrease indicates that the reactive surface, hence the water sediment transport, was limiting for nitrate removal of the overlying solution.

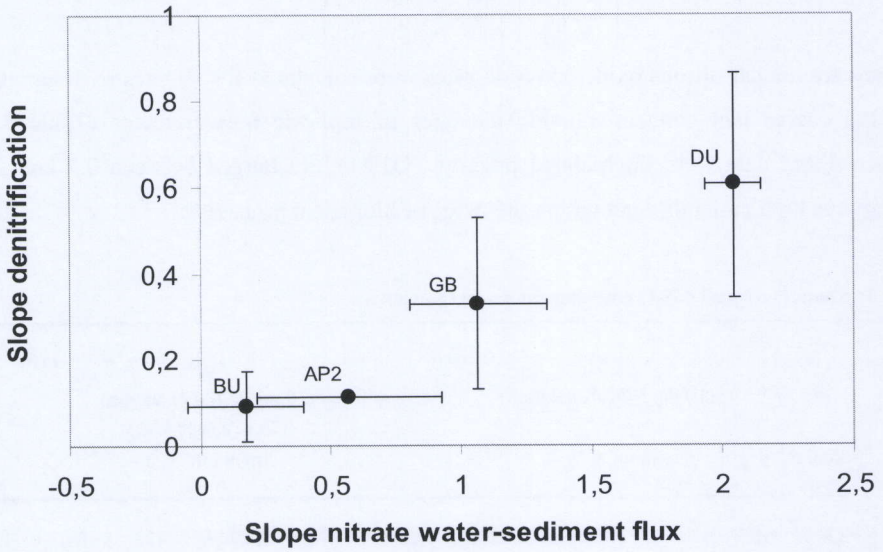


Fig. 5.5: Slope of denitrification vs. nitrate water sediment flux at increasing overlying nitrate solutions (0, 1, 5 and 10 mg N L^{-1}); replicates over the nitrate concentration gradient: $n_{DU} = 3$, $n_{AP2} = 2$, $n_{BU} = 2$, $n_{GB} = 2$. Slopes were determined on individual regression lines of the flux rates (in mmol m^{-2} d^{-1}) at increasing nitrate concentrations and then averaged over the different experiments.

Emission of nitrous dioxide did not show a similar increase as in Fig. 5.5 (data not shown); slopes ranged from -0.03 to 0.16 (R^2 from 0.32 to 0.77).

Amendment with glucose on replicate samples (addition of 10 mg N L^{-1} only) of the N vs. C limitation experiment did not lead to any change in nitrate water-sediment flux rates after the first day of incubation (paired T-test, performed on individual nitrate water-sediment flux rate slopes with and without glu amendment for the stations Durme, Appels 2, Burcht and Groot Buitenschoor, t=0.86, p=0.89, n=4). These results show that nitrate availability, not carbon, was the limiting factor for denitrification in the Scheldt sediments.

5.3.4 Oxygen consumption experiment

Oxygen consumption was highest in sediment of the Durme and lowest in sediment of Appels 3 (Table 5.4). Addition of 100 individual oligochaetes on sediment of AP3 (experimental sediment surface = 15.8 cm^2) resulted in a change from zero order to a polynomial decrease

(Fig. 5.6). Given an oxygen consumption rate increase from 0.48 to 8.33 μg $O_2.cm^{-2}$ h^{-1} (Table 5.4), the oxygen consumption of one average Oligochaete amounted to 1.2 μg O_2 h^{-1}., corresponding with a consumption rate of 1.23 mol O^2.mol C^{-1} d^{-1}.

Table 5.4: Oxygen removal rates of mudflat sediment

Station	Rate (mg O_2 cm^{-2} h^{-1})	n
GB	1.3 ± 0.5	2
BU	2.3 ± 1.2	2
DU	7.9 ± 1.8	5
AP 2	2.0 ± 1.0	2
AP3	0.5	1
AP3+100 Oligochaetes	8.3	1

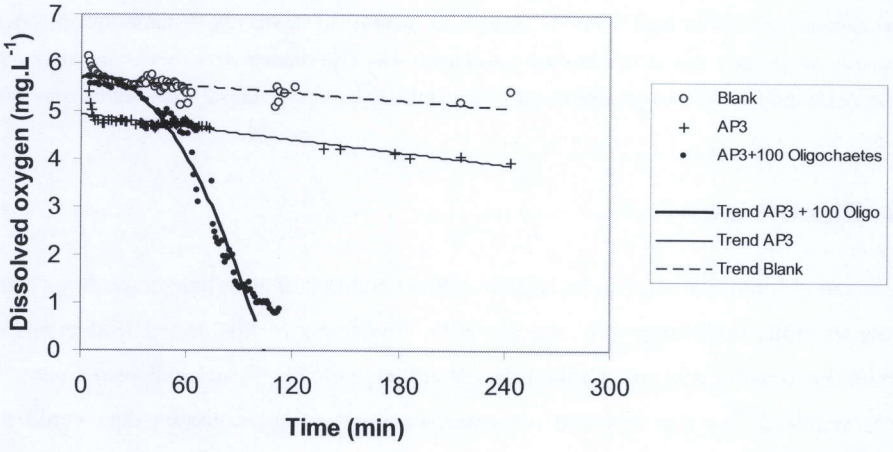


Fig. 5.6: Dissolved oxygen concentration in overlying water of sediment with and without addition of 100 Oligochaetes; blank = water without sediment or Oligochaetes

5.3.5 Experimental tidal mudflat

Denitrification in sediment, exposed after submersion by 10 $mg.L^{-1}$ nitrate solution, and under 10 kPa acetylene incubation, decreased exponentially with time (Fig. 5.7). At a high tide - low tide regime of 2h - 10 h, the measured denitrification rate decreased to zero after 8 to 9 hours, whereas at the 6h-6h regime, the slope of the exponential curve did not reach zero at the end of the low tide. This pattern was repeated over 3 tides (data not shown). Organic

matter was not the limiting factor in the decrease, as the N_2O concentrations in the head space continued to increase after consequent low tide phases (Fig. 5.7).

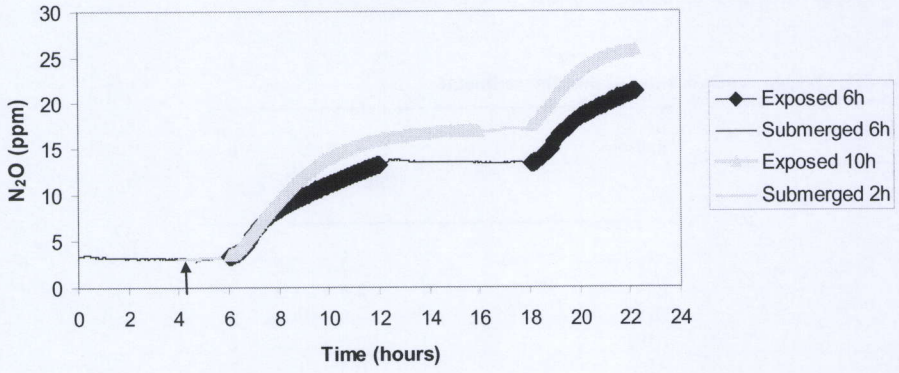


Fig. 5.7: Comparison of N_2O concentrations in the flux chamber of the tidal experiment container under two tidal regimes: 6 hours low tide - 6 hours submersion with 10 mg L^{-1} NO_3^--N, and 10 hours low tide - 2 hours submersion with 10 mg L^{-1} NO_3^--N. Before the measurements were recorded the meso-system was allowed to adapt for 1 day to the imposed conditions. The experiments were carried out under 10 kPa acetylene incubation. The arrow indicates the start of the 10 hours low tide - 2 hours submersion run.

5.4 Discussion

Nitrous oxide emission rates were, with or without addition of acetylene in the flux chambers, highly variable, both temporally and spatially, confirming in this aspect Middelburg *et al.* (1996). Seasonality was only partly apparent although the Q_{10} values indicated a temperature effect (Table 5.2). The temporal or spatial variation of the emission data could not be explained by any combination of variables.

5.4.1 Denitrification

The observed denitrification rates (Table 5.2) were for the corresponding locations (Durme and Burcht) an order of magnitude lower than the denitrification rates estimated by Middelburg *et al.* (1995b). Middelburg *et al.* (*op cit.*) calculated nitrification coupled denitrification at low tide, while in our approach acetylene inhibited nitrification in submerged sediment. According to a review of Seitzinger *et al.* (1988), nitrification in sediments is in most estuaries the major source of nitrate for sediment denitrification; denitrification resulting from overlying nitrate being about ten times lower than nitrate

coupled denitrification. This is confirmed by our denitrification results: they are one order of magnitude lower than the nitrification supported denitrification values of Middelburg *et al.* (1995b), while the agreement with the diffusion supported fraction is good: 0.50 mol m^{-2} y^{-1} for Doel which is comparable with our values of the nearby station of Groot Buitenschoor. There was also agreement with the modelled results of Soetaert & Herman (1995).
Laverman *et al.* (2007), who combined the acetylene technique with microsensor measurements on sediment of Appels, found depth integrated denitrification values of 12 mmol N m^{-2} d^{-1} which is much more than our values of 0.22 to 6.8 mmol N m^{-2} d^{-1}. These values, however, represent potential rates, stimulated by flow through conditions (Laverman *et al.*, 2006). High denitrification values (up to 13.8 mmol N m^{-2} d^{-1}) were recorded for intertidal freshwater sediments of the Yorkshire Ouse, using the acetylene inhibition technique (Garcia-Ruiz *et al.*, 1998). The global averaged system denitrification values (adding up both nitrification and overlying nitrate as sources) of estuaries (about 1 mmol N m^{-2} d^{-1}, excluding fresh water zones) and rivers (about 2 mmol N m^{-2} d^{-1}), as reviewed by Seitzinger *et al.* (2006), indicate that denitrification in the Scheldt, according to any author, is intensive.

The nitrate load leaving the Zeeschelde amounted in the early 1990's to 9000 tons per year (Soetaert & Herman, 1995). Based on our data, extrapolated linearly for the pelagic nitrate concentrations (as recorded by Van Damme *et al.*, 2005) by using the slopes of Fig. 5.5, and by using the compartments proposed by Soetaert & Herman (*op cit.*), the mudflats of the Sea Scheldt could only eliminate 0.6% of this load by diffusion supported denitrification. Despite the intensity of the process, diffusion supported denitrification in mudflats constituted a marginal effect on the nitrogen budget of the estuarine system. Including also nitrification supported denitrification, Middelburg *et al.* (1995b) estimated that intertidal sediments might account for 14% of the total estuarine nitrogen retention, making abstraction of possible annamox bias. The recent evolution of the water quality (Cox *et al.*, 2009), indicates that despite the recovery of the oxygen status, the nitrate concentration continues to decrease so that diffusion supported denitrification will decrease with it, as nitrate was the limiting factor for denitrification. At constant nitrate availability, however, the N_2O emission rate decreased as the inundation period and concurrent tidal submersion level increased (Fig. 5.7), although the headspace concentration continued to increase. The depth profiles of Laverman *et al.* (2007) show similar patterns at some mm in depth, as the pore water concentration increased with inundation time, but at the surface the production rate did not significantly change.

The stimulating influence of benthos, and more specifically of Oligochaetes, on denitrification has already been reported (Chatarpaul *et al.*, 1980; Pelegri and Blackburn 1995). This was explained by enhanced water-sediment transport. The peaking values of denitrification in the sediment of the Durme (Fig. 5.2) were registered when this station was characterised by a massive presence of oligochaetes. On this location, Seys *et al.* (1999) found an average benthos density of 243400 ind. m^{-2} which was about 4 times more than the average density in the entire Zeeschelde. It was noted that the abundant benthos community in the Durme site was removed by local dredging after the month of August, which could explain the lower denitrification values in the Durme in October (Fig. 5.2). In order to further assess the impact of the benthos, comparative oxygen consumption rates were measured. The sediment oxygen consumption increase after addition of 100 individual oligochaetes was of the same range as the difference between the oxygen consumption rates of the Durme and the other stations (Table 5.4). The benthos oxygen consumption recorded in this study (1.23 mol O^2 mol C^{-1} d^{-1}), was more than 3 times larger than given by the benthos respiration formula at 25°C in the model of Soetaert *et al.* (1995). This indicates that the enhanced denitrification rates of the Durme station are probably linked with benthos activity, not only through enhanced exchange of nitrogen, but also because the benthic activity lowered the oxygen content of the sediment surface layer.

5.4.2 Global warming

The *in situ* N_2O emission rates at low tide (Table 5.2) were up to 4 times higher than the corresponding values found by Middelburg *et al.* (1995b): as indicated in their paper, their values could have been higher if they had applied longer accumulation times in the incubation chamber.

The emissions of N_2O were compared with other sources of greenhouse gas emissions in the Schelde. The global warming potential of CO_2, CH_4 and N_2O (ratio 1:23:296), was multiplied with the according annual emission rates, in order to rank the importance of the emissions per surface unit according their contribution to global warming (Fig. 5.8). This comparison revealed that CO_2 is by far the most important contributor the greenhouse problem when compared with CH_4 and N_2O. Only in the freshwater tidal flats, enormous CH_4 emissions that were recorded by Middelburg *et al.* (1996) in the Durme tributary caused CH_4 to be the dominant greenhouse gas (18 times the reference). These high values were not reported

elsewhere in the freshwater part (Siebens, 1997). The peculiar aspect of the Durme station, as described earlier, is likely to be not representative for the freshwater part of the Schelde.

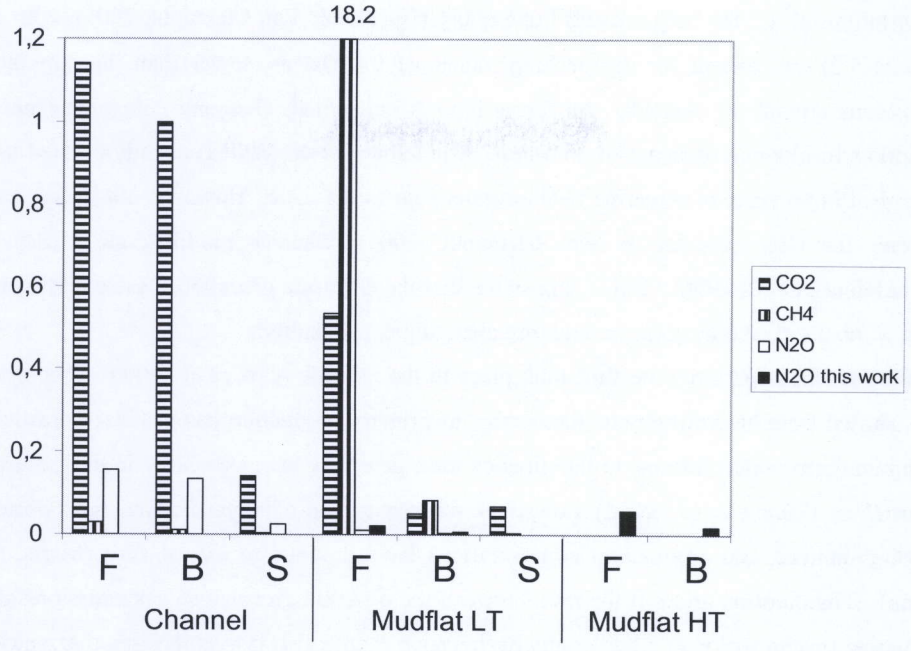


Fig. 5.8: Relative contribution of greenhouse gas emission fluxes of the Schelde to global warming potential per surface unit for different compartments of the Scheldt estuary, compared to the CO_2 GWP of the brackish channel compartment, set as reference value 1, as measured during the period 1993-1997 (channel = pelagic + subtidal sediment); F = salinity 0-2, B = salinity 2-15, S = salinity > 15, LT = low tide, HT = high tide. Sources: CO_2 channel: Frankignoulle *et al.* (1996); CH_4 channel: Middelburg *et al.* (2002), fluxes calculated with piston velocity of 8.4 cm.h^{-1} as determined by Frankignoulle *et al.* (1996); N_2O channel: De Wilde & de Bie (2000); CO_2 and CH_4 mudflat: Middelburg *et al.* (1996); N_2O mudflat: Middelburg *et al.* (1995b) and this work. For Mudflat HT only data of this work (N_2O) are available.

Nitrous oxide emission from the water surface contributed 5 (fresh water part) to 13 times (brackish and saline part) more to global warming than emission of CH_4. In mudflats at low tide, on the contrary, emission of N_2O contributed marginally in comparison to CO_2 and CH_4. For mudflats at high tide, no CO_2 or CH_4 emission data were available to compare with the higher N_2O emissions. Our data indicated that emission of N_2O from exposed tidal flats were an order of magnitude lower than emission from the water surface according to De Wilde &

de Bie (2000). As the mudflat surface becomes submerged, the emission values shifted more to those of the water surface above the subtidal system compartment.

The average N_2O emission from cultivated land is 101 mmol m^{-2} y^{-1} for the Netherlands and 76.4 mmol m^{-2} y^{-1} for Belgium and Luxemburg (Boeckx & Van Cleemput, 2001). Our data (Table 5.2) are, except for the peaking values of the Durme, lower than the agricultural emissions around the Scheldt. As far as N_2O is concerned, changing cultivated land into mudflats results in a decrease of emission. Middelburg *et al.* (1995a) already pointed to the marginal importance of estuarine N_2O emissions on world scale. However, cultivated land is a sink for CH_4 (Boeckx & Van Cleemput, 2001), whereas mudflats are clearly not (Middelburg *et al.*, 1996). But it is possible that the estuarine greenhouse gas emission rates that were observed during the nineties are changing considerably.

During recent years a regime shift took place in the Schelde (Cox *et al.*, 2009). The system has shifted from heterotrophy to autotrophy, as primary production has increased drastically. While oxygen concentrations in the nineties were generally low, especially in the freshwater zone (Van Damme *et al.*, 2005), nowadays supersaturation of oxygen is regularly observed during summer, and ammonium concentrations have dropped to almost zero (Maris, pers. com.). The question arises if the ratio between the different greenhouse gas emissions of the estuarine system will alter significantly during such changes. It is hypothesised that, since the nineties, emission of CO_2 and CH_4 has shifted from the estuarine system to water treatment plants, offering technical possibilities to capture CH_4. If the hypothesis is true it can be concluded that restoring estuarine ecological habitats by creating more intertidal areas cannot be compromised by pointing to the medal backside of enhancing greenhouse gas emission.

Acknowledgements

This study was funded within the OMES project by the Flemish Environmental Agency (VMM). We thank the Flemish Administration for Waterways and Maritime Affairs, division Zeeschelde for the field support.

Chapter 6

Tidal exchange between a freshwater tidal marsh and an impacted estuary (Scheldt estuary, Belgium)

Van Damme S., Dehairs F., Tackx M., Beauchard O., Struyf E., Gribsholt B., Van Cleemput O. & Meire P.

Estuarine, Coastal and Shelf Science 85: 197-207 (2009)

Abstract

Tidal marsh exchange studies are relatively simple tools to investigate the interaction between tidal marshes and estuaries. They have mostly been confined to only a few elements and to saltwater or brackish systems. This study presents mass balance results of an integrated one year campaign in a freshwater tidal marsh along the Scheldt estuary (Belgium), covering oxygen, nutrients (N, P and Si), carbon, chlorophyll, suspended matter, chloride and sulphate. The role of seepage from the marsh was also investigated. A ranking between the parameters revealed that oxygenation was the strongest effect of the marsh on the estuarine water. Particulate parameters showed overall import. Export of dissolved silica (DSi) was more important than exchange of any other nutrient form. Export of DSi and import of total dissolved nitrogen (DIN) nevertheless contributed about equally to the increase of the Si:N ratio in the seepage water. The marsh had a counteracting effect on the long term trend of nutrient ratios in the estuary.

6.1 Introduction

It is generally thought that fringing marshes act as a filter for the estuarine water by removing inorganic and organic substances from the floodwaters or by changing the substance speciation (*e.g.* Cai *et al.* 2000; Tobias *et al.*, 2001; Gribsholt *et al.*, 2005). The marsh basically provides a large increase in reactive surface and enhances sedimentation. In the past, the interaction between tidal marshes and estuaries or coastal zones received much attention through numerous exchange studies (*e.g.* Valiela *et al.*, 1978; Spurrier & Kjerfve, 1988; Whiting *et al.*, 1989; Jordan & Corell, 1991; Childers *et al.*, 1993). In these 'classic' interaction studies, fluxes were determined through the construction of mass balances. Dominant questions were whether marshes were importing or exporting substances, such as N, P, C or particulate matter (C and sediment), often testing the 'outwelling' hypothesis (*e.g.* Dame *et al.*, 1986). Recently these studies have shifted their focus towards the underlying processes, using more refined techniques such as isotope labeling (*e.g.* Gribsholt *et al.*, 2005, 2006). However, there are several reasons why exchange studies within the frame of the eutrophication problem in estuaries and coastal seas are still important.

Firstly, while certain aspects such as P and N retention (*e.g.* Valiela *et al.*, 1978; Dame *et al.*, 1986; Whiting *et al.*, 1989; Jordan & Corell, 1991; Troccaz *et al.* 1994) have been studied in detail, others such as Si have been covered less frequently (*e.g.* Dankers *et al.*, 1984; Struyf *et al.*, 2005). The high input of N and P in estuaries can lead to potential Si limitation in diatom communities, which are then less available to the higher trophic levels than dominating non-diatom species (Schelske *et al.*, 1983; Smayda, 1997). Silica has only exceptionally been incorporated in mass balance studies (*e.g.* Dankers *et al.*, 1984; Struyf *et al.*, 2005). Furthermore, while tidal salt marshes are relatively well studied (*e.g.* Troccaz *et al.* 1994) only few mass balance studies have focused on freshwater tidal marshes (*e.g.* Simpson *et al.*, 1983; Childers & Day, 1988; Bowden *et al.*, 1991; Struyf *et al.*, 2005 & 2006, Gribsholt *et al.* 2005, 2006). With their botanical properties resembling inland freshwater wetlands, and as they interact more with river hydrology and the corresponding water quality than saline marshes, freshwater tidal marshes are very specific process interfaces. Within these potentially strongly reactive areas, it has been shown through process studies that the seepage water, that usually contributes a minor part of the tidal water balance

of the marsh, nevertheless can play a very important role in the processing capacity of a marsh. Yet the characterization of the seepage water has in the classic mass balance studies only seldom been emphasized (*e.g.* Whiting & Childers, 1989).

Secondly, most tidal marsh exchange studies were performed in the 1970s and 1980s. For many estuaries, this period was characterized by peaking eutrophication problems. This is notably true for *e.g.* the Seine (Billen & Garnier, 1999), the Elbe (ARGE – Elbe, written communication) and the Scheldt estuary (Soetaert *et al.*, 2005). In the 1990s, measures were generally taken to improve the water quality and, as a consequence, river scientist are now often studying "oligotrophication" (decreasing N and P loads) rather than eutrophication. Thus, potential nutrient limitation in estuaries has changed, especially in the Scheldt estuary, where the N:P Redfield ratio, charcterising the need for growth of diatoms, shifted from less than 20 in the seventies to over 50 in 2000 (Billen *et al.*, 2005; Van Damme *et al.*, 2005, Soetaert *et al.*, 2006). In the Seine, a similar phenomenon was documented (Billen *et al.*, 2001). It is interesting to investigate if such a trend in estuarine systems interacts with the processing potential of marshes. Therefore a re-assessment of tidal marsh exchange is required, illustrating the use of old unpublished data.

Nutrient regulation, oxygenation, sediment accretion, carbon production and processing and water storage are all directly or indirectly linked with ecological functions or goods and services of estuarine systems, as defined *e.g.* by De Groot *et al.* (2002). The use of ecosystem functions in estuarine restoration has the major advantage that it is not a static approach, as is much of the protective legislation. The aim of this study was to assess the interaction of a freshwater tidal marsh and the water column by means of mass balances, including a comparison between nutrients, carbon, suspended matter and other parameters. This comparison is a basic essential step in the quantification and decision making of priorities in estuarine restoration. Also, the difference between the bulk tidal exchange and seepage is scoped.

In this study fluxes of nutrients (N, P and Si), carbon and particulate matter were determined in a freshwater tidal marsh, together with the ambient estuarine conditions. Also the oxygenating potential, the fluxes of chloride and sulphate, and other supporting parameters were determined simultaneously. To our knowledge, this is a tidal marsh exchange study with the most comprising parameter list so far.

6.2 Material and methods

Four mass-balance studies were conducted in a freshwater tidal marsh of the Scheldt estuary: on 1 July 1997, 7 October 1997, 27 January 1998 and 29 April 1998. Each tidal cycle was monitored at the entrance of the main creek as well as in the river upstream of the marsh. The cycles were monitored from the point of low tide in the river to the next low tide. All 13 hour measurement campaigns started between 12:30 and 16:00.

6.2.1 Site description

The Scheldt estuary extends from the mouth in the North Sea at Vlissingen (km 0) till Gent (km 160), where sluices and weirs stop the tidal wave in the Upper Scheldt (Fig. 6.1). The tidal wave also enters the major tributaries Rupel and Durme, providing the estuary with approximately 235 kilometres of tidal river. The Zeeschelde (105 km long) is characterized by a single ebb/flood channel, bordered by relatively small mudflats and marshes (28% of total surface). The basic features of the Scheldt estuary are described in more detail elsewhere (Meire *et al.*, 2005).

The selected area is a freshwater tidal marsh (surface approximately 92.000 m^2), situated at Tielrode near the mouth of the Durme tributary which is silted up in a high degree (Fig. 6.1). The marsh is surrounded by dikes. At the landside a winter dike is elevated 8m above average low water level; at the riverside a summer dike is 2m lower than the winter dike. At present, the vegetation of the marsh is dominated by a patchy pattern of osier thicket (dominated by Salix sp.), reed (*Phragmites australis*) and tall herb vegetation (characterized by *Urtica dioica*, *Epilobium hirsutum* and *Impatiens glandulifera*). A single creek has developed, from a breach in the winter dike, as the major access from the river to the marsh. The creeks and lower parts of the marsh are flooded by a semidiurnal tide while the highest parts are only flooded by spring tides. A bridge was installed over the main creek at the riverside, from which all sampling took place. The geometry of the cross section of the creek, coated with stone rubble, was measured twice consecutively by means of a teodolite (Fig. 6.2).

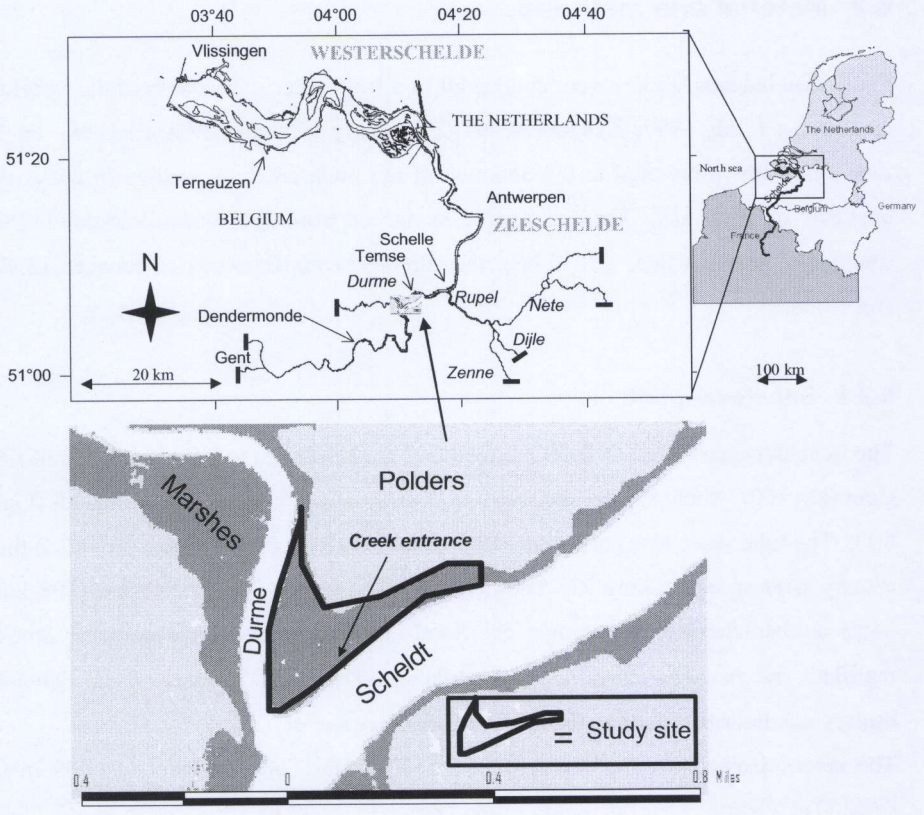


Fig. 6.1: Map of the Scheldt estuary, with the investigated study site

6.2.2 Water balances

Discharged volumes were calculated by multiplying flow velocity measured every two minutes and cross section area during the bulk tidal phase and every half hour during the seepage water phase. The bulk tidal phase is here defined as the period during which large amounts of water flow in and out (flood and ebb) the marsh through the main creek. The bulk tidal phase started when the rising tide entered the creek through the sampling transect (Fig. 6.2). The seepage phase started per definition when the water height in the creek dropped below approximately 30 cm depth at the deepest point of the creek transect.

During the bulk phase, water flow velocity was measured continuously over the cross surface (about 30 m^2) at 2 m width and 0.5 m depth intervals (Fig. 6.2), using 4 'OTT'-mill flow velocity meters which could rotate on a vertical axis to determine the

angle of the water flow relative to the banks. Thus, temporal, vertical and horizontal flow variations were covered. The 'seepage' flow was measured chronographically in 30-minute intervals by following floating coarse particulate debris that flowed over a known distance in a straight stretch. Water height was recorded in the centre of the creek approximately every two minutes in the bulk tidal phase and every half hour during the seepage phase.

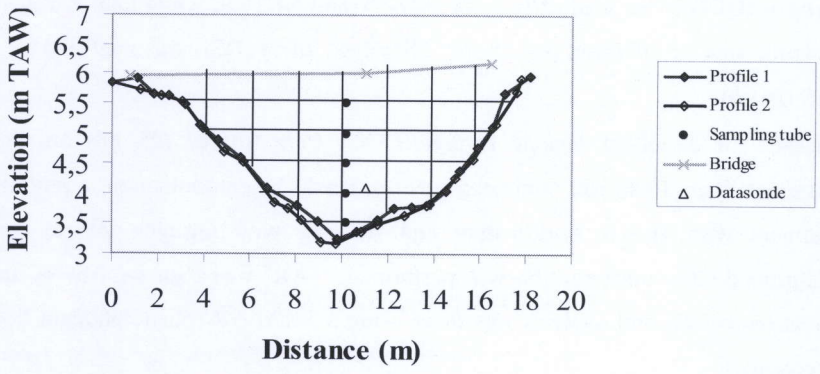


Fig. 6.2: Geometry of the cross section of the main creek (two profiles). At the crossing of horizontal and vertical grid lines, current velocity was measured. (Sampling tube = location where water samples were taken; Datasonde = location of the datasonde; Bridge = level of the walking board over the creek)

The water balances were corrected for precipitation which fell during the tidal cycle when relevant, using the data of the nearby weather station of Bornem of the Belgian Royal Meteorological Institute. The correction of the water balance was done by adding the precipitation mass over the marsh area to the mass of the flood phase.
Data interpolations were performed using a simple model, as in Struyf *et al.* (2006).

6.2.3 Sampling and analysis

Water samples were collected at 0.5 m depth intervals along the vertical gridline in the centre of the creek (Fig. 6.2) using a handpump that was connected to sampling pipes. The sampling pipes were attached in a vertical tube and reached out through openings at the depth intervals. Samples were collected every half hour during the bulk tidal phase at each depth (when flooded).

Water samples (250 ml) for Cl^- (included in the study as a tracer), NH_4^+-N, NO_3^--N , NO_2^--N, Kjeldahl N, dissolved inorganic phosphorous (DIP), total phosphorous (Tot P), dissolved silica (DSi) and SO_4^{2-}-S were stored at 4°C and were analyzed within 24h after sampling. Analysis of Cl^-, NO_3^--N, NO_2^--N, NH_4^+-N, SO_4^{2-}-S, DIP, Kjeldahl-N (after oxydation in H_2SO_4) and Tot P (after oxydation in H_2SO_4 and $K_2S_2O_8$) was done using a SKALAR SA 5100 segmented flow analyzer. Organic N was calculated by subtracting NH_4^+-N from Kjeldahl-N. Total dissolved inorganic nitrogen (DIN) is the sum of NO_3^--N, NO_2^--N and NH_4^+-N, while total nitrogen (tot N) is the sum of DIN and organic N. Dissolved silica (DSi) was analyzed by ICP-OES (Iris®).

Samples for dissolved organic carbon (DOC) were filtered (25 ml) on Gelman glassfiber filters (0.45 µm nominal porosity). For DOC determination, a preliminary treatment with H_2SO_4 acidification and flushing with nitrogen gas to remove background CO_2 concentration was performed. DOC was then set free by further oxidation to CO_2 and analysis was done using a SKALAR (phenolphtalein 550 nm detection).

Suspended particulate matter (SPM) was determined gravimetrically after filtration (25 ml) on pre-combusted Whatman GF/F 0.7 µM filters, previously dried at 60°C. Particulate organic carbon (POC) and particulate nitrogen (PN) were determined after filtration on pre-combusted Whatman GF/F 0.7 µM filters, using a Carlo Erba CN analyzer NA 1500 after Cr_2O_3 and $AgCo_3O_4$ catalyzed oxidation and segregation on a Haysep-Q-column.

Particulate total carbon (PTC) and particulate inorganic carbon (PIC) were analyzed by use of carbon analyser Ströheim Model Coulomat 70I LI, using heating at 900°C and an acid medium (*i.e.*, 85% orthophosphoric acid, ortho-H_3PO_4 plus 15% silver nitrate, $AgNO_3$) to convert respectively PTC and PIC to CO_2 which was quantified by automatic coulometric titration of alkaline barium perchlorate $(Ba(ClO_4))_2$ solution. The Coulomat was standardised with $CaCO_3$. The particulate organic carbon (POC) content in the samples was obtained by subtracting the values for PIC from those of respective PTC.

Water samples for chlorophyll (100 ml) were filtered on pre-combusted 45µ Sartorius filters and frozen at -20°C immediately afterwards. Pigments were extracted in 90%

acetone and quantified using high pressure liquid chromatography according to Wright *et al.* (1991).

A Water Quality Multiprobe Hydrolab H20®, measuring oxygen saturation every 5 minutes, was installed in the center of the creek (Fig. 6.2) under the water surface during the bulk tidal phase. In the seepage phase, samples were collected with the cup of the multiprobe and immediately fixed on it for measurement.

River water was collected from a boat with a 15 L Niskin bottle for analysis of the same parameters as mentioned above (incl. handling and analysis). The boat was positioned in the middle of the river before the marsh entrance. Temperature and oxygen content of the river were measured *in situ* with a 'WTW OXI 91' oxygen-meter.

Statistics were performed using S-Plus 2000.

6.2.4 Balances of dissolved and particulate matter

Transport of dissolved and particulate material was calculated by multiplying discharge with measured concentrations throughout the tidal cycles. Weighted average concentrations per tidal cycle phase (bulk inflowing, bulk out flowing and seepage phase) were calculated as the ratio of the total amount of transported matter and the amount of water discharged during a particular tidal phase.

Nutrient balances were rendered conservative by correcting for the import or export of water (by subtracting percentage import/export of water from percentage matter exchange). In a conservative mass-balance, it is assumed that there was no net import or export of water (Dankers *et al.*, 1984). This correction was necessary to allow comparison between tidal cycles, which differ in the ratio of imported and exported water volumes (Fig 3).

6.3 Results

6.3.1 Water balances

The discharge profiles of the four monitored cycles showed a similar pattern (Fig. 6.3). It took a few hours before the rising tide reached the level of the breach where the creek starts. During this period, water from the previous tide still seeped out of

the marsh. During flood the discharge increased to a maximum after which it slowed down till slack tide. Superimposed on the tidal discharge asymmetry pattern, as described by Postma (1967), the out flowing water showed an additional discharge peak when the level of the river surface dropped below the level of the creek. Only in April were the two peak discharge patterns smoothed out by the high discharge values. The vertical distribution of the inflow was less homogenous than of the outflow; the lateral distribution of the stream velocity showed an asymmetrical pattern (data not shown).

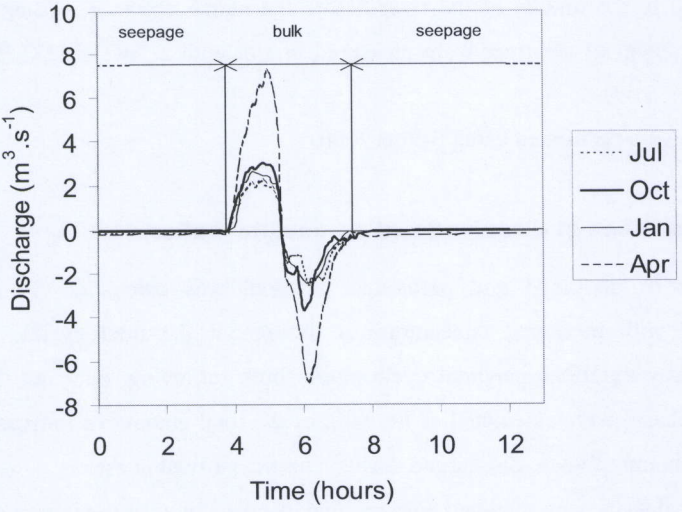


Fig. 6.3: Water discharge through the main creek for each measured tidal cycle (Jul = July 1997, Oct = October 1997, Jan = January 1998, Apr = April 1998)

Inflowing and out flowing water volumes were nearly equal during 3 out of the 4 studies (Table 6.1). The exported water volume greatly exceeded the inflowing volume in April. Here the exchanged water volume was more than double than that of October, although the water level reached was only 8 cm higher. A possible reason is that water that entered the marsh during the previous tidal cycle had not completely flowed out of the marsh yet. This is more likely to occur at higher tides (Dankers *et al.*, 1984), which was the case for the April 1998 cycle (Table 6.1). It was also noticed that at this higher tide the river water was at some locations flowing over the worn out crown of the summer dike. It is also likely that the marsh, while still not fully flooded through the main access channel, was flooded by water that in a diffuse way flowed over the dike, and that the subsequent drainage occurred predominantly

through the main channel, thus creating strong ebb current. This phenomenon also often occurs in coastal zones and is known as 'rip currents'.

Table 6.1: Water balances for all tidal cycles conducted, with separate indication of seepage-, bulk inflowing and bulk out flowing water. The net balance is also indicated in percent of the inflow (% of In) Maximal water height is expressed in cm TAW, the Belgian national tidal reference (indicating a historic low tide average at Antwerpen). The average discharge of the decade preceding each tidal cycle is given for Schelle; precipitation data provided by the belgian Royal Meteorological Institute.

Date	Max. Height	Bulk water mass		Seepage		Precipitation	Balance Out-In*	
		Incoming	Out going					
	(cm)	(m^3)	(m^3)	(m^3)	(% of total out going)	(m^3)	(m^3)	(% of In)
01/07/97	541	9834	9601	750	7.5	368	149	2
07/10/97	562	12649	11415	1090	8.7	0	-144	-1
27/01/98	533	10221	9843	99	1.0	0	-279	-3
29/04/98	570	26221	23501	5845	19.9	0	3125	12

*: positive value = export, negative value = import

Precipitation was only recorded during the July campaign, where 4 mm of rain fell just after high tide. In January, air temperature dropped below zero, so that an unknown mass of water froze onto the marsh surface. This amount was probably very limited as the flood level was then quite low.

The exchanged water volumes were small compared to the long term averaged discharge of 100 $m^3\ s^{-1}$ of the Scheldt estuary at Schelle, situated 10 km downstream of the sampling site (Fig. 6.1). The yearly average of 1997 and 1998 was 84 and 135 $m^3\ s^{-1}$ respectively.

6.3.2 Concentrations and mass balances

Some features of the Scheldt estuary can readily be recognized in the data. The tidal marsh of Tielrode is situated in the oligohaline zone (0.5 – 5 PSU) of the Scheldt estuary, which is reflected in the tidal maxima of chloride and sulfate (Table 6.2). The marsh is furthermore situated upstream the Rupel tributary, discharging untreated wastewater from the city of Brussels. The tidal action dissipates this load up till and even far upstream the sampling site. This is reflected in the water quality patterns of the Scheldt estuary (Van Damme *et al.*, 2005): At high tide, minimal concentrations were observed in the river for DO and NO_3^--N, and maxima for NH_4^+-N.

Table 6.2: Concentrations and mass balances (+ = export, - = import) for all parameters and for each studied tidal cycle. Shown concentration values include river values, averaged for low tide (LT) and high tide (HT), and minimal and maximal values of the seepage phase. If a homoscedastic single T-test, comparing the chronological first half with the second half of the seepage phase samples ($n \geq 8$), was significant ($p \leq 0.05$), then an arrow indicates if the concentration pattern of the seepage phase goes from maximum to minimum or vice versa. The mass balances is shown with separate indication of seepage-, bulk inflowing and bulk out flowing water. The net balance (Out-In) is also given per marsh area unit and in percent versus the inflow (% of In). (Cons. = conservative net balance (in % according to the inflow), *i.e.* corrected for import or export of water, DO = Dissolved oxygen, SPM = suspended matter, DIN = total dissolved nitrogen, org N = organic nitrogen, PN = particulate nitrogen, tot N = total nitrogen, tot P = total phosphorous, DSi = dissolved silica, DOC = dissolved organic carbon, POC = particulate organic carbon, PIC = particulate inorganic carbon, PTC = particulate total carbon, Chl a = chlorophyll a, Chl b = chlorophyll b)

Par.	Month	Concentrations					Mass Balance					Cons.
		River		Seepage		Incoming	Outgoing			Out-In		Out-In
		LT (*)	HT (*)	min (*)	max (*)	Bulk (**)	Bulk (**)	Seepage (**)	(**)	(***)	(% of In)	(% of In)
Cl^-	Jul	2.7	4.7	3.5 →	4.1	1119	1252	105	238	2.58	21	20
	Oct	16	37	22 ←	24	13200	13011	906	717	7.80	5.4	6.6
	Jan	2.0	3.2	2.5 →	3.0	915	938	9.6	33	0.36	3.6	6.4
	Apr	2.5	3.1	2.3 →	2.6	2217	2414	528	725	7.89	33	21
SO_4^{2-}	Jul	1.0	0.88	1.1 →	1.1	918	881	77	40	0.44	4.4	2.8
	Oct	1.6	2.2	1.9 ←	2.2	2505	2430	209	134	1.46	5.3	6.5
	Jan	1.2	1.1	1.2	1.2	1119	1079	11	-28	-0.31	-2.5	0.2
	Apr	1.2	0.93	1.1 →	1.1	2618	2236	529	147	1.60	5.6	-6.3
DO	Jul	0.03	0.02	0.13	0.17	7.0	13	3.6	10	0.11	143	141
	Oct	0.16	0.01	0.17	0.18	7.7	14	6.1	12	0.13	154	155
	Jan	0.23	0.18	0.37 →	0.43	80	83	1.3	4.6	0.05	5.7	8.4
	Apr	0.07	0.01	0.13	0.16	8.8	45	28	64	0.69	723	712
SPM	Jul	63	28	34 ←	128	1214	956	82	-176	-1.91	-14	-16
	Oct	97	66	42 ←	200	4277	3272	260	-745	-8.10	-17	-16
	Jan	192	22	28 ←	214	1554	985	14	-555	-6.03	-36	-33
	Apr	179	18	14 ←	104	3781	3363	313	-105	-1.14	-2.8	-15
NH_4^+-N	Jul	0.29	0.34	0.11 ←	0.14	48	44	1.2	-2.7	-0.03	-5.6	-7.1
	Oct	0.00	0.15	0.03 →	0.05	23	22	0.5	-0.3	0.00	-1.1	0.0
	Jan	0.19	0.24	0.08 ←	0.11	30	28	0.1	-1.6	-0.02	-5.3	-2.5
	Apr	0.15	0.20	0.02 ←	0.05	55	55	1.7	1.8	0.02	3.3	-8.6
NO_3^--N	Jul	0.15	0.08	0.12 ←	0.20	20	16	1.5	-2.1	-0.02	-10	-12
	Oct	0.37	0.18	0.16 ←	0.26	37	32	3.3	-2.1	-0.02	-5.8	-4.6
	Jan	0.54	0.42	0.50 ←	0.57	70	66	0.8	-2.5	-0.03	-3.6	-0.9
	Apr	0.40	0.31	0.37 ←	0.43	139	114	33	8.6	0.09	6.2	-5.7

Table 6.2: Continued

Par.	Month	Concentrations				Mass Balance						Cons.
		River		Seepage		Incoming	Outgoing			Out-In		Out-In
		LT (*)	HT (*)	min (*)	max (*)	Bulk (**)	Bulk (**)	Seepage (**)	(**)	(***)	(% of In)	(% of In)
NO_2^--N	Jul	0.01	0.03	0.01 ←	0.01	1.3	2.2	0.1	0.9	0.01	65	63
	Oct	0.01	0.02	0.00 ←	0.00	3.0	2.7	0.1	-0.2	0.00	-8.2	-7.1
	Jan	0.01	0.01	0.01 →	0.02	5.9	4.1	0.0	-1.8	-0.02	-30	-28
	Apr	0.02	0.03	0.00 ←	0.01	9.4	8.7	0.3	-0.4	0.00	-4.5	-16
DIN	Jul	0.46	0.44	0.24 ←	0.34	69	63	2.8	-3.9	-0.04	-5.6	-7.1
	Oct	0.39	0.35	0.19 ←	0.31	63	56	3.9	-2.7	-0.03	-4.2	-3.1
	Jan	0.75	0.67	0.59 ←	0.70	106	99	0.9	-5.9	-0.06	-5.6	-2.9
	Apr	0.57	0.53	0.40 ←	0.49	202	177	35	10	0.11	4.9	-7.0
Org N	Jul	0.17	0.11	0.13 ←	0.26	27	22	1.7	-2.7	-0.03	-10	-12
	Oct	0.11	0.00	0.10 ←	0.17	27	22	1.7	-3.3	-0.04	-12	-11
	Jan	0.09	0.04	0.06 ←	0.19	21	16	0.2	-5.4	-0.06	-25	-23
	Apr	0.14	0.09	0.06 ←	0.09	48	42	6.7	1.1	0.01	2.3	-9.6
PN	Jul	0.05	0.04	0.00	0.00					0.00		
	Oct	0.07	0.04	0.08 ←	0.16	27	21	1.4	-4.2	-0.05	-16	-15
	Jan	0.09	0.03	0.02 ←	0.09	9.5	7.0	0.1	-2.4	-0.03	-25	-23
	Apr	0.06	0.02	0.01 ←	0.05	36	22	2.1	-12	-0.13	-32	-44
Tot N	Jul	0.63	0.55	0.37 ←	0.60	96	85	4.5	-6.6	-0.07	-6.9	-8.4
	Oct	0.50	0.36	0.29 ←	0.48	89	78	5.5	-6.0	-0.06	-6.7	-5.5
	Jan	0.84	0.71	0.64 ←	0.88	127	115	1.1	-11	-0.12	-8.9	-6.2
	Apr	0.71	0.62	0.46 ←	0.58	250	220	42	11	0.12	4.4	-7.5
PO_4^{3-}-P	Jul	0.04	0.02	0.04 →	0.05	5.0	4.2	0.5	-0.2	0.00	-4.9	-6.5
	Oct	0.04	0.03	0.03 →	0.04	6.7	6.3	0.6	0.2	0.00	2.3	3.4
	Jan	0.03	0.02	0.03 →	0.04	3.2	3.1	0.0	-0.1	0.00	-1.6	1.1
	Apr	0.02	0.02	0.03	0.04	7.6	6.3	3.0	1.7	0.02	22	10
Tot P	Jul	0.07	0.04	0.09 ←	0.23	14	9.8	1.3	-3.1	-0.03	-22	-23
	Oct	0.07	0.03	0.08 ←	0.15	28	21	1.5	-5.3	-0.06	-19	-18
	Jan	0.05	0.03	0.05 ←	0.13	12	8.4	0.1	-3.4	-0.04	-28	-26
	Apr	0.06	0.03	0.04 ←	0.07	28	25	3.9	0.5	0.01	1.8	-10
DSi	Jul	0.15	0.15	0.24 →	0.28	50	50	6.5	5.7	0.06	11	9.8
	Oct	0.10	0.11	0.24 →	0.28	52	51	9.1	8.0	0.09	15	17
	Jan	0.20	0.20	0.21 →	0.24	65	63	0.7	-1.4	-0.02	-2.1	0.6
	Apr	0.16	0.17	0.22 →	0.28	138	127	50	39	0.42	28	16
DOC	Jul	0.29	0.28	0.16 →	0.20	33	37	1.6	5.6	0.06	17	16
	Oct	0.41	0.31	0.18 →	0.30	49	41	2.7	-5.7	-0.06	-12	-10
	Jan	0.04	0.12	0.16 →	0.24	23	24	0.2	1.8	0.02	8.0	11
	Apr	0.18	0.71	0.58	0.69	302	214	47	-41	-0.45	-14	-25
POC	Jul	0.43	0.33	0.83 ←	3.0	113	83	5.2	-25	-0.27	-22	-24
	Oct	0.66	0.43	0.58 ←	0.87	219	167	13	-39	-0.42	-18	-17
	Jan	1.0	0.19	0.12 ←	0.98	82	60	0.8	-21	-0.23	-26	-23
	Apr	0.89	0.17	0.18 ←	0.65	283	197	19	-66	-0.72	-23	-35
PIC	Jul	0.03	0.02	0.07 ←	0.47	11	9.2	0.8	-1.2	-0.01	-11	-13
	Oct	0.08	0.06	0.08 ←	0.22	39	30	3.7	-5.4	-0.06	-14	-13
	Jan	0.14	0.02	0.02 ←	0.13	16	11	0.2	-5.0	-0.05	-31	-28
	Apr	0.15	0.05	0.02 ←	0.07	71	43	3.9	-24	-0.26	-34	-46
PTC	Jul	0.47	0.36	0.90 ←	3.5	124	92	6.0	-26	-0.28	-21	-23
	Oct	0.74	0.49	0.67 ←	1.1	258	197	16	-44	-0.48	-17	-16
	Jan	1.2	0.21	0.13 ←	1.1	98	71	0.9	-26	-0.29	-27	-24
	Apr	1.0	0.22	0.20 ←	0.72	354	240	23	-90	-0.98	-26	-37

Table 6.2: Continued

Par.	Month	Concentrations				Mass Balance						Cons.
		River		Seepage		Incoming	Outgoing			Out-In		Out-In
		LT (*)	HT (*)	min (*)	max (*)	Bulk (**)	Bulk (**)	Seepage (**)	(**)	(***)	(% of In)	(% of In)
Chl a	Jul	63	63	63	63	1209	968	17	-224	-2.43	-19	-20
	Oct	63	63	63	63							
	Jan	4.3	1.1			32	19					
	Apr	63	63	4.0 ←	63	931	837	50	-44	-0.48	-4.8	-17
Chl b	Jul	6.3	6.0	4.6	7.3	64	56	0.6	-7.8	-0.08	-12	-14
	Oct	6.9	2.6									
	Jan	0.30	0.02			3.4	0.4					
	Apr	1.7	0.80	0.10 ←	1.3	47	42	1.7	-3.7	-0.04	-7.8	-20

* : Concentration unit: mM except for SPM (mg L^{-1}) Chl a and Chl b (mg L^{-1})
**: Mass unit: kg except for Chl a and Chl b (g)
***: Unit: g m^{-2} except for Chl a and Chl b (mg m^{-2})

Over all months, consistent import or export was noted for 13 of the 17 independent (in the sense of not calculated from others) parameters (Fig.4). Dissolved oxygen, DSi and chloride were exported in all cases, while SO_4^{2-}-S showed mostly export with only slight import in April. Import was observed in all cases for NH_4^+-N, NO_3^--N, hence also for DIN. Parameters from the particulate phase (SPM, Chl a and b, PN, PIC, POC, PTC) and also organic N, Tot N and Tot P showed import in all cases.

Of all campaigns, the results of the winter were distinct. In January, export in general was marginal (Fig. 6.4). The marsh surface was then frozen, which was apparently blocking most seepage (Table 6.1). Import, however, was noted for SPM, PN, PIC, Tot P, POC and organic N, as the frost did not prevent deposition of particulate matter (Fig. 6.4).

The export of DO was the clearest observed phenomenon. In April, a sevenfold export amount was recorded, while in the other seasons except winter, oxygen also showed top export rates of well over 100% (Fig. 6.4). For DO, the seepage phase contributed more to the mass balance than for any other parameter, except in January (Fig. 6.5) when the river concentrations were high.

Chloride concentrations in the river were much higher in October than in any other month, despite the fact that the water level was higher at high tide in April (Table 6.2). This can be explained by the discharge in October, which was almost three times lower than in April (Table 6.1). The salinity gradient along the estuary showed in October 1997 an intrusion of about 20 km more upstream as compared with April 1998 (Van Damme *et al.*, 2005). Sulfate showed similar patterns.

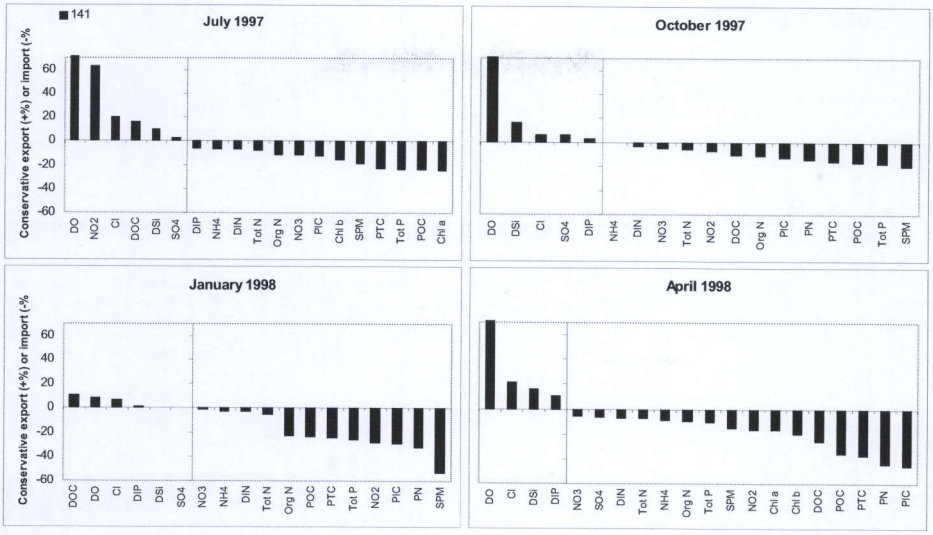


Fig. 6.4: Conservative import (negative value) or export (positive value), *i.e.* corrected for import or export of water, for all measured parameters and for each tidal cycle (DO = dissolved oxygen, Cl = chloride, DOC = dissolved organic carbon, DSi = dissolved silica, SO4 = sulfate, DIP = dissolved inorganic phosphorous, tot P = total phosphorous, NH4 = ammonium-N, NO3 = nitrate N, NO2 = nitrite-N, DIN = total dissolved nitrogen, tot N = total nitrogen, org N = organic nitrogen, PIC = particulate inorganic carbon, POC = particulate organic carbon, PTC = particulate total carbon, SPM = suspended matter, chl a = chlorophyll a, chl b = chlorophyll b)

Parameters from the particulate phase (SPM, Chl a and b, PN, PIC, POC, PTC) and also organic N, Tot N and Tot P showed similarity in the concentration pattern: At the end of the bulk out flowing phase and the beginning of the seepage phase, concentrations peaked to reach the maximal value of the whole profile (Table 6.2, detail pattern not shown). Despite this peak there was always a net import, because the high concentrations in the bulk out flowing phase were linked with lower discharges than the bulk inflowing phase (Fig. 6.3; Table 6.1). Also, without exception, the seepage phase of these parameters showed clear decreasing profiles, so that the seepage phase showed always depletion relative to the bulk out flowing phase, except for PIC and Tot P in July, and for some parameters in January, when the marsh was frozen and the seepage water showed only minor difference with the bulk out flowing phase (Fig. 6.5). There was no consistent ranking between the parameters of the particulate phase concerning shifts in SPM composition from bulk water to

seepage water: POC accounted for 2.1 - 26.5 % of SPM (8.3 ± 2.7 %), and for 73 - 98 % of PTC (88 ± 3 %).

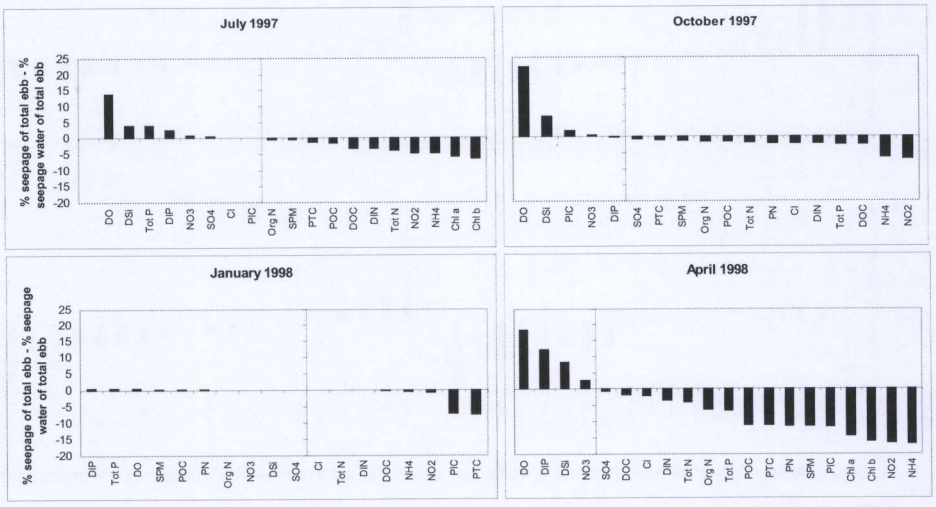


Fig. 6.5: Difference (in %) between export in the seepage phase of any measured physicochemical parameter and export of water in the seepage phase (DO = dissolved oxygen, Cl = chloride, DOC = dissolved organic carbon, DSi = dissolved silica, SO4 = sulfate, DIP = dissolved inorganic phosphorous, tot P = total phosphorous, NH4 = ammonium-N, NO3 = nitrate N, NO2 = nitrite-N, DIN = total dissolved nitrogen, tot N = total nitrogen, org N = organic nitrogen, PIC = particulate inorganic carbon, POC = particulate organic carbon, PTC = particulate total carbon, SPM = suspended matter, chl a = chlorophyll a, chl b = chlorophyll b)

The components of Tot N (NH_4^+-N, NO_3^--N, NO_2^--N and org N) behaved differently. In terms of percentage the import of NO_3^--N was maximal (Fig. 6.4) when the concentration in the river was lowest, *i.e.* in July (Table 6.2). On the contrary, in January, when NO_3^--N concentrations in the river were highest, the net import was relatively low, despite the high amounts that were exchanged. NH_4^+-N on the other hand showed largest import when the concentrations in the river were high, and lowest import at the lowest concentrations, *i.e.* in October. The seepage phase was, relative to the bulk out flowing phase, in all cases enriched with NO_3^--N and depleted of NH_4^+-N. The concentration profile of the seepage phase was for nitrate and ammonium always decreasing, except in October, when an increase of ammonium was recorded (Table 6.2). The import of NO_3^--N was thus due to the bulk phase, the seepage phase even somewhat counteracting the import (Fig. 6.5), while for NH_4^+-N

the seepage phase played a more important role. Org N accounted for 16.8 - 37.8 % of Tot N. The exchanged PN amounted between half and completely the corresponding amount of org N (Table 6.2).

Of all N-parameters, only NO_2^--N showed both export and import (Fig. 6.4). The export/import ratio for nitrite was predominantly determined by changes in the bulk tidal phase (Table 6.2). The seepage phase was, compared with the bulk out flowing phase, consistently depleted of nitrite. However, the fact that nitrite showed both export and import is made less important in view of that constituents consistently low concentrations.

DIP was one of the four elements not showing consistent import or export in the four measured tidal cycles. Import occurred in July and export in the three other months (Fig. 6.4). In three of four cases, the seepage phase showed highest concentrations of DIP. Lowest concentrations were measured at high tide in the river (Table 6.2).

DSi concentrations were highest in the seepage phase, showing strong increase (Table 6.2). In July, October and April the DSi enriched seepage water contributed more to the overall out flowing DSi budget than any other parameter but DO (Fig. 6.5). The export in these months could be attributed to these high amounts of DSi in the seepage phase (Table 6.2). Clearly the winter situation was totally different from the other seasons (Table 6.2; Fig. 6.4), showing some import and a constant concentration level throughout the tidal cycle. DSi was the only of all parameters to show this particular behaviour, which was with these data for the first time observed for tidal marshes. The concentration profiles and balances of DSi are therefore presented in more detail and extent elsewhere, pointing at the concentration increase in the seepage phase in comparison with patterns in a saline marsh (Struyf *et al.*, 2005). Here, the focus is pointed at the relation with the other nutrients.

6.3.3 Nutrient ratios

The molar ratios of N:P (Fig. 6.6) and Si:N (Fig. 6.7) delivered by the marsh are important because they show how the marsh influences the elements that control estuarine and eventually marine phytoplankton. In all cases, the N:P ratio of the seepage phase dropped below the values of the river, reaching the lowest values in July and October (Fig. 6.6). In these months the seepage phase nutrient ratios showed potential N limitation.

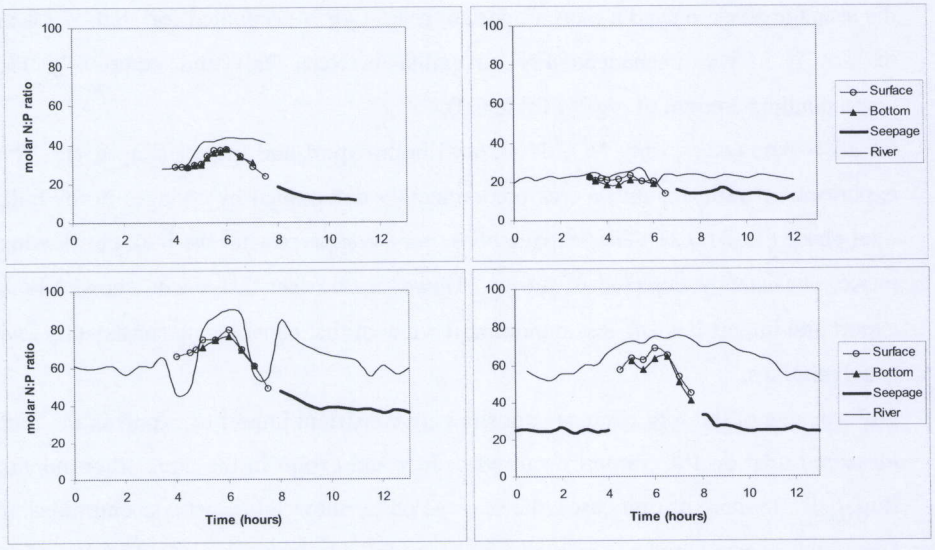


Fig. 6.6: Variations of the N:P ratio during the conducted tidal cycles. The Redfield ratio characterising the need for diatom growth is indicated in the dashed line.

The Si:N ratio (optimal 1:1) of the river water was confined between 0.2 and 0.4, except in January, when a maximum of 0.57 was reached (Fig. 6.7). In July, October and April the Si:N ratio increased strongly in the seepage phase, exceeding the river values clearly, and lifting the ratio beyond potential Si limitation. In January the increase of Si:N in the seepage phase was very moderate, hardly exceeding the river values, and the N:P ratio in the seepage phase was then relatively high, compared to the other months.

6.3.4 Contribution of the changes in the seepage phase to the balance

In July and October, the strongest positive influence of the seepage phase on the net balance was found for parameters of the dissolved phase: DO, DSi, ammonium and DIN (Fig. 6.8). In October larger contributions were found than in July. Parameters of the particulate phase added less than 1% to the net balance or counteracted it maximum 2%. For DIP the enrichment of the seepage phase counteracted the net (non conservative) balance, except in April. In January, limited contribution was noted, as the seepage was hardly differentiated from the bulk phase (Fig. 6.5), and the balances were relatively conservative compared to the other months (Fig. 6.4). In April, strong effects on the net balance took place, 34% of the SPM import was due to

depletion of SPM in the seepage phase, while the counteracting effects mounted up to over 50% for Tot P. For chloride, only a relative strong effect was seen in October, when the tidal variation was high.

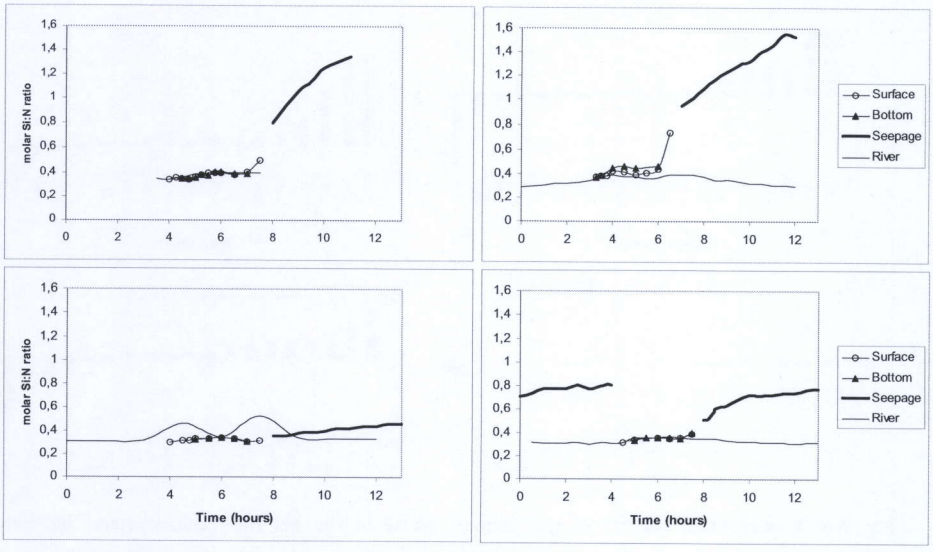


Fig. 6.7: Variations of the Si:N ratio during the conducted tidal cycles. The Redfield ratio characterising the need for diatom growth is indicated in the dashed line.

6.4 Discussion

Before addressing the aims of this study (the effect of the marsh, the comparison between parameters and the difference between the seepage and bulk phase) the quality of the data must be assessed. Indeed, the water vs. the chloride balances showed differences that could indicate error. However, the concentration profiles indicate that the marsh can to some degree load and unload salt. Sediment physical properties, evapotranspiration and elevation are important determinants of salinity variation in pore water (Morris, 1995). This confirms that it is unsuitable to use chloride as a conservative tracer in single tidal exchange studies. Spurrier & Kjerfve (1988) calculated that at least 34 cycles need to be measured in order to quantify the error of tidal exchange balances. This implies that the error of the presented 4 balances remains unclear. The mass balances in April were probably biased by a rip current. In the three other cases the water balances showed less than 3% imbalance,

which is a very good fit for traditional mass balance studies, if compared with other studies (*e.g.* Dankers *et al.*, 1984; Gribsholt *et al.*, 2005).

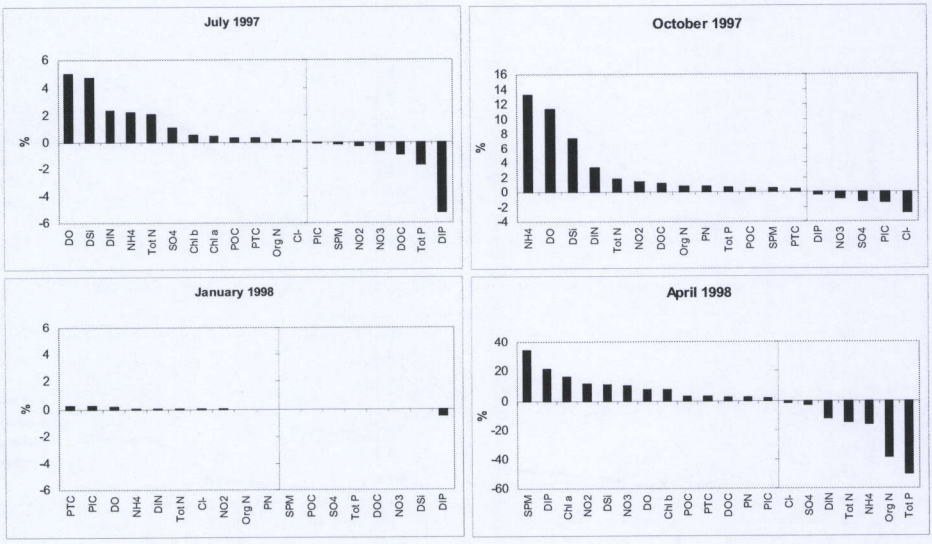


Fig. 6.8: Contribution (in %) of the seepage phase to the net (non conservative) balance, determined through comparing the net total balance with a conservative and a non conservative seepage phase. Positive values mean that the seepage added up to the net import or export. Negative values mean that the seepage counteracted the net import or export. (DO = dissolved oxygen, Cl = chloride, DOC = dissolved organic carbon, DSi = dissolved silica, SO4 = sulfate, DIP = dissolved inorganic phosphorous, tot P = total phosphorous, NH4 = ammonium-N, NO3 = nitrate N, NO2 = nitrite-N, DIN = total dissolved nitrogen, tot N = total nitrogen, org N = organic nitrogen, PIC = particulate inorganic carbon, POC = particulate organic carbon, PTC = particulate total carbon, SPM = suspended matter, chl a = chlorophyll a, chl b = chlorophyll b)

The oxygenating effect was the most conspicuous impact of the marsh on the flood water. In the river, the main source of aeration is input from the atmosphere (Soetaert & Herman, 1995). On the marsh, this is different, since in a shallow layer of flooding water, primary production is not hampered by light limitation as it is in the river. The residence time of the water on the marsh surface is too low to allow much local pelagic or benthic primary production that could explain the oxygenation. Besides, during all campaigns except in July, the seepage phase was predominantly sampled overnight. The oxygenation is due to the physical process of gas exchange with the atmosphere, as the oxygen poor water extends over the marsh surface in a shallow

layer. As such, freshwater tidal marshes provide oxygen to the estuary, especially when the oxygen demand is high. This pattern was also observed by Gribsholt *et al.* (2006).

Import of nitrate and ammonium was per square meter of the same order of magnitude than in other in freshwater tidal areas (Simpson *et al.*, 1983; Childers & Day, 1988; Bowden *et al.*, 1991). In a 3477 m^2 corner of the Tielrode marsh, the fate and transport of ammonium was quantified in two whole-ecosystem $15N\text{-}NH_4^+$ labeling experiments in May 2002 and September 2003, showing that nitrification was one of the most important transformation processes, accounting for 17 - 32 % of the transformed label (Gribsholt *et al.*, 2006). This confirms our findings that the seepage water was somewhat enriched in nitrate and depleted of ammonium. Only a small amount of denitrification was found by Gribsholt *et al.* (2005), which seems in discordance with the import of DIN. It could be that in the labeling studies, denitrification was underestimated, as some 14% of the label was not found back, and the denitrification appeared more important when the label was added in a higher degree (Gribsholt *et al.*, 2006).

The high chlorinity in October can explain the increase of ammonium during the seepage phase, which was recorded only then. It has been shown that salinity increases from 0 to 10 PSU, corresponding with the observed chloride increase, can markedly decrease the ammonium adsorption capacity of sediment, thus releasing it in the seepage water (Rysgaard *et al.*, 1999).

The results indicated export for carbon. Although the sampling method was probably not adequate to collect all of the coarse vegetation debris that was floating around, especially during the high flooding in April, the seepage phase was depleted of particulate carbon. DOC on the other hand showed export. The role of primary production on the marsh is ambiguous. Carbon is produced by marsh plants, and storm events can have a drastic effect on the export of this production (*e.g.* Roman & Daiber, 1989), but vegetation also stimulates sedimentation of particulate matter (Rooth *et al.*, 2003). The import rates of SPM correspond with sedimentation rates between 0.84 $kg.m^{-2}.a^{-1}$ in April and 5.91 $kg.m^{-2}.a^{-1}$ in October. These relatively low values are typical for old, elevated marshes (Temmerman *et al.*, 2005), such as the Tielrode marsh.

Silica plays a key role in the symptoms of eutrophication of coastal waters (Smayda, 1997). In the lowest reaches of the Scheldt estuary silica can be limiting for diatom blooms (Van Spaendonk *et al.*, 1993). Therefore the observed export of the marsh needs attention. Clearly the winter situation was totally different from the other seasons (Fig. 6.4-5), showing some import and a constant concentration level throughout the tidal cycle. The export values of the other seasons (Table 6.2) correspond with 4-27 mM $Si.m^{-2}.d^{-1}$, taking into account a marsh surface of 10 ha. These values are much higher than the modelled mass transfer between muddy sediment and water (1.7 mM $Si.m^{-2}.d^{-1}$) in the adjacent coastal zone (Vanderborght *et al.*, 1977). Increasing salinity is associated with higher silica dissolution (Yamada & d'Elia, 1984), so the salinity gradient is unlikely to explain the higher fluxes in the marsh. Efflux of silicic acid from sediments has been shown to be dependent on biogenic (*i.e.* diatom) deposition (Yamada & d'Elia, 1984). Drying creeks at low tide may well act as a trap for diatoms. The high export rates are probably related to regeneration of deposited biogenic matter. The fact that no export was noted in winter, when diatoms are nearly absent (Muylaert *et al.*, 2000), sustains this hypothesis.

The export of DSi is only one aspect of the silica processing of the marsh. Struyf *et al.* (2006) revealed that the strong export of DSi is a result of the recycling of imported biogenic silica in the marsh. The import that was found for chlorophyll is in accordance with these findings, as this suggests that diatoms are imported to the marsh. The processing of Si in the marsh is, however, not at all restricted to diatom recycling; vegetation, especially reed (*Phragmites australis*) plays a major role in transforming BSi to DSi (Struyf *et al.*, 2005).

Tidal input/output studies are a relatively simple tool to combine several aspects of ecological functioning of marshes, offering possibilities not only to compare them, but also to rank them in order of importance regarding their effect. This can only be achieved if standards for comparison are available, for instance in the form of ecological objectives. These are in the process of construction, but already the nutrient ratios provide opportunities to assess the relative importance of estuarine immissions.

A modeled reconstruction of the water quality history showed that in the seventies, when the water quality was very deteriorated, yearly values of N:P near the marsh (Temse) were below 16 (Billen *et al.*, 2005). Since then the ratio showed an increase

to more than 60 at the end of the nineties. The Si:N ratio decreased from more than 1 in the beginning of the fifties to less than 0.4 at the end of the nineties. These results are confirmed by the observed trends in the downstream part of the estuary: the Western Scheldt. Here the N:P ratios more than doubled from 1980 to 2002, due to the differences in the reduction rate of DSi (1.2% yr^{-1}), DIN (1.7% yr^{-1}), and DIP (5.4% yr^{-1}), while the Si:N ratio varied from 0.2 to 0.4 (Soetaert *et al.*, 2006). These trends were attributed to more DSi retention in the drainage network as its quality gradually improved, and the human effort to restore water quality by water treatment plants, resulting in higher efficiency in reducing the P load, as it originates mainly from point sources (Billen *et al.*, 2005). The studied marsh had a decreasing effect on the N:P ratio, counteracting in fact the increasing trend in the estuary. This is because the marsh is relatively more efficient in transforming N than P, when compared with the human effort, thus providing a measure to restore water quality that is complementary to the effect of water treatment plants. Also the negative Si:N trend in the estuary was countered by the marsh, even in a stronger way, as DSi and DIN contributed both and about equally to the increase of the ratio in the seepage water.

The nutrient ratios in the Scheldt showed seasonal variation: In the estuary, near the marsh, the N:P ratio ranged in 1997-1998 between roughly 100 in winter and 20 in summer and Si:N between 0.5 in winter and 0.2 in summer (Van Damme, unpublished results). The results of the river profiles reflect these variations, meaning that in summer, nitrogen limitation can still occur, and that potential DSi limitation is prominent year round and is maximal in summer. The marsh had its most prominent effect on the Si:N ratio (Table ratio) when the concentrations of both DIN and DSi in the river were low (Table 6.2).

Primary production in the Scheldt estuary is, however, not primarily limited by nutrients, but by light (Soetaert *et al.*, 1994). Although it is known that nearly all the sediment input from the watershed results from anthropogenic activities such as tillage (Van Oost *et al.*, 2000; Van Rompaey *et al.*, 2001), the relation between estuarine hydrology and SPM concentration is not yet fully understood. Therefore it is not possible to assess the importance of marshes in trapping sediment.

Acknowledgements

The results were sponsored by the Flemish Environmental Agency (VMM) and the Flemisch Administration for Waterways and Maritime Affairs, division Zeeschelde. We thank the Fund for Scientific Research for funding the Scientific Community 'Ecological characterization of European estuaries, with emphasis on the Schelde estuary' (project nr. W 10/5 - CVW.D 13.816).

Chapter 7

Using carrying capacity compensation scenarios to quantify ecological conservation objectives for mudflats: a general approach applied on the Zeeschelde (Scheldt estuary, Belgium)

Van Damme S., Billen G., Cox T., Van den Bergh E., Ysebaert T., Jacobs S., Maes J., Maris T. & Meire P.

Abstract

Designating restoration goals for dynamic systems like estuaries requires intrinsic flexibility in the restoration concept as well as an expression of the restoration goals in manageable units. An approach is presented to obtain quantified estuarine conservation objectives, using carrying capacity as a central concept. Different scenarios were constructed based on trophic relations, area availability and waste loads. The distinction between 'good' reference and 'bad' compensative scenarios was determined through criteria concerning species diversity. The approach was applied on the Belgian part of the Scheldt estuary, the Zeeschelde. In the Zeeschelde, dissolved oxygen was the first limiting factor on diversity. Using a catchment model in combination with the diversity restrictions, reference scenarios revealed themselves as a pristine scenario and a scenario representing the waste load situation of the year 1950. It was calculated that the Zeeschelde needs about 500 ha extra mudflat area to compensate for lost macrobenthic production. Waste load reductions were also proposed, taking into account catchment derived nutrient ratios.

7.1 Introduction

In and around the estuaries of the developed world and especially of NW-Europe, space is highly demanded for various societal needs. Most estuaries harbour harbours as gates of commerce and trade that feed industry and densily populated areas around them. Agriculture is intense and land prices are in general relatively high. How much area of a habitat is needed? This question is often uttered by policy makers and ecosystem managers who need to budget spatial resources.

Amidst a whole range of such society relevant functions, estuaries support many functions that are more closely related to the system itself: biogeochemical cycling and movement of nutrients, purification of water, mitigation of floods, maintenance of biodiversity, biological production, etc. (Meire *et al.*, 2005). Many functional needs can be translated into physical entities. Water storage capacity volumes can be calculated as a function of flood risk, harbour space as a function of traffic needs, etc. It is of crucial importance that ecological needs can likewise be translated to manageable units such as space.

In Europe the recognised ecological value of estuaries is crystallised in protective legislation. The European Bird Directive (79/409/EEG) and Habitat Directive (92/43/EEG) are important juridical imperatives providing protected areas in estuaries. For areas under the Habitat Directive a good state of conservation is required. Therefore every member of the European community is bound to construct Conservation Objectives that guarantee the presence of the protected habitats and viable populations on the long term. The Water Framework Directive (2000/60/EG) requires that a good ecological status for transitional and coastal waters must be reached in 2015. The ecological status must be formulated based on phytoplankton, macro-algae, angiosperms, benthic invertebrates and fish. This status must be evaluated against a (theoretical) undisturbed reference condition (*e.g.* Borja *et al.*, 2000).

Conservation objectives can be very strong instruments, linking the present and potential ecological health with clear management objectives, provided that they are well constructed. However, construction of conservation objectives or reference conditions for estuarine habitats faces complications, as estuarine habitats are far from static. These transitional water systems are geomorphologically very dynamic and ephemeral, influenced both by sea and land changes, forming a complex and ever evolving mixture of many different habitat types, exposed to human induced changes in water quality and various other kinds of disturbances (Meire *et al.*, 2005) According to the dominating flow pattern, mudflats can either erode to

subtidal areas or change into pioneering marshes, young marshes can grow old and old marshes can drown by erosion (Van de Koppel *et al.*, 2005). As the restless nature of estuaries also persists in the long run, both natural evolution and human impacts are intertwined as causes of morphological transition. As such it becomes impossible to refer to a temporal reference state '*sensu stricto*' in order to assess the ecological condition of an estuary. Within this fluid framework, the quantification of habitat needs requires an approach transcending ambiguities resulting from static '*hic et nunc*' protective recommendations.

Up till now, conservation objectives for estuarine systems have only been expressed in general terms, *e.g.* stating that parameters should not deviate significantly from an established base line, subject to natural change (Elliott, University of Hull, written communication, 2008). Such an approach is depending on the definition of 'baseline' and the interpretation of 'significantly', complicating in this way the objectivity of the approach. Up till now conservation objectives of estuarine habitats, expressed in manageable units, have never been reported. It is the double challenge of this article to 1) overcome the issue of system dynamism in expressing conservation objectives and 2) to express conservation objectives in quantified terms of space so that they are easily feasible for management. It is the aim of the present paper to present a coherent method or approach to derive such conservation objectives. Although elaborated for the Zeeschelde, the Belgian part of the Scheldt estuary, we believe that the approach is applicable not only on this selected case but on many estuaries.

First, the outline of the conceptual approach is explained. Then the approach is applied on the well documented Zeeschelde.

7.2 Conceptual approach

7.2.1 Conservation objectives, carrying capacity, ecosystem functioning and space

How much area of a habitat is needed? The question contains the presumption that space is the main determinant of a good state of the habitat, *i.e.* its production, quality and the diversity of the life it carries. This is true for certain environments (Paine, 1966), but certainly not all. The definition of conservation objectives requires that the system can sustain itself and that the populations that live in it are viable on the long run. The concept of carrying capacity is closely related to this formulation of objectives. Many definitions of

carrying capacity have been elaborated (overviews *e.g.* in del Monte-Luna *et al.*, 2004 and Elliott *et al.*, 2007). Carrying capacity was formerly and more usually used as an ecological concept but it is extendable in terms of both environmental and societal demands *i.e.* what the natural system wants and can accommodate and what are society's aspirations (Cohen, 1997; Elliott & Cutts, 2004; MacLeod & Cooper, 2005; Yozzo *et al.*,, 2000; Van Cleve *et al.*, 2006), or to system function, ecosystem goods and services, as listed by De Groot *et al.* (2002). The choice of definition depends on what we want to consider for restoration and conservation. Keeping in mind that the eventual results must be expressed in function of area, then the classic definitions are suitable like *e.g.* from Baretta-Bekker *et al.* (1998): 'the maximum population size possible in an ecosystem, beyond which the density cannot increase because of environmental resistance'. It is synonymous with the general productivity of an ecosystem. However, when linking the concepts of carrying capacity and conservation objectives, discordance emerges. Conservation objectives require the determination of minimal conditions for a system to be sustainable, while carrying capacity is about determining maximal possible entities that can be sustained. But the fact that carrying capacity is not a constant on the long term (Seidl and Tisdell, 1999) can be used to develop conservation scenarios. It is in our approach assumed that carrying capacity is a constant during a five year period, and that five year period scenarios can be compared as different states of equilibrium. The strength of linking the carrying capacity and conservation objective concept is that they both share the same duality: not only the production, population, standing stock, crop or other entities that are scoped, need to be considered, but also the factors that control them and that affect quality. The challenge is to assemble all quality needs in the population or production size calculations, and to quantify these relations from the viewpoint of spatial aspects.

7.2.2 Mudflats and benthos

Mudflats are very illustrative for the dynamic and ephemeral character of the estuarine ecosystem. Their outline is set vaguely by the level of high and low water, which probably contributed to the fact that mudflat area evolution is less documented than that of tidal marshes (Meire *et al.*, 2005). Nevertheless, according to De Groot *et al.* (2002) mudflats have important functions. They reduce dike abrasion by wave action, dissipate tidal energy and are potential hot spots for denitrification (Middelburg *et al.* 1996). They host a major part of the estuarine benthic invertebrates (Ysebaert *et al.*, 2005), supporting numerous overwintering wading-birds and different guilds of adult and juvenile fish. The production of benthos is

crucial for these higher trophic levels, and this function is the epicentre of our approach. Carrying capacity of wading birds is not scoped as its determination is more complicated than for benthos. The development of competitive interference between wading birds has indicated that food resource competition alone underestimates the demands for space (Stillman *et al.*, 2005). Furthermore it is assumed that the ecotrophic efficiency, *i.e.* the fraction of the benthos production that is utilized within the system for predation or export (Christensen & Pauli, 1998), is a fix percentage of production for all scenarios.

The carrying capacity (CC) for higher trophic levels (waders, fish) in an estuarine ecosystem, depends on the biomass of benthic invertebrates as the maximal system averaged standing stock, is expressed as:

$$CC = B*A \qquad (1)$$

with A the total system habitat area, and B the system averaged benthic biomass per area unit, resulting from all factors of which it is influenced. We assume a linear relation between carrying capacity and habitat area, restricting our approach to the many cases where mudflats are fringing habitats. Both mudflat area and benthic biomass are not constant in time. Mudflat area is prone to morphologic evolution, land reclamation etc., benthic biomass can alter under different water and sediment quality factors. In this approach we assume that all changes in carrying capacity result from human interference. By putting the natural carrying capacity as a constant 'pristine state', it becomes possible to budget changes. The carrying capacity between two scenarios can be thus be compared as:

$$B_i * A_i = B_j * \left(A_j + A_c\right) \qquad (2)$$

with i a reference scenario and j a scenario to be assessed (Fig. 7.1). One scenario covers a five year period in which a carrying capacity equilibrium is assumed. A scenario can be situated in the present, the past or the future. The equation is matched by the area compensation term A_c. A_c represents the area that is needed to compensate scenario j for scenario i. The following scenarios were selected:

- The 'pristine' scenario represents a hypothetical state of the Scheldt basin before any significant human disturbance. It corresponds to a watershed entirely covered by forest.

Low soil leaching and erosion as well as direct litter fall in the tributaries are the only external inputs of nutrient considered. This scenario stands for the 'very good' state of the estuary. The mudflat area is for this scenario unknown.

- The scenarios '1950' to '2000' consist of a reconstruction of the evolution of agriculture, industrial and urban wastewater management policies over the last 50 years, as explained in detail by Rousseau *et al.* (2005). The time range covers the evolution to the worst water quality ever recorded for the Scheldt and its subsequent recovery (Soetaert *et al.*, 2006).
- The '2015' scenario is a prospective scenario assuming that the requirements of all European directives on wastewater treatment and water management are met everywhere in the basin. In particular, this scenario takes into account a 90% abatement of the organic load of urban wastewater by secondary treatment, and an abatement of 90% of the phosphorus load and 70% of the nitrogen load by tertiary treatment. This scenario represents, admittedly, a quite optimistic view of the future situation of the Scheldt hydrographic district.

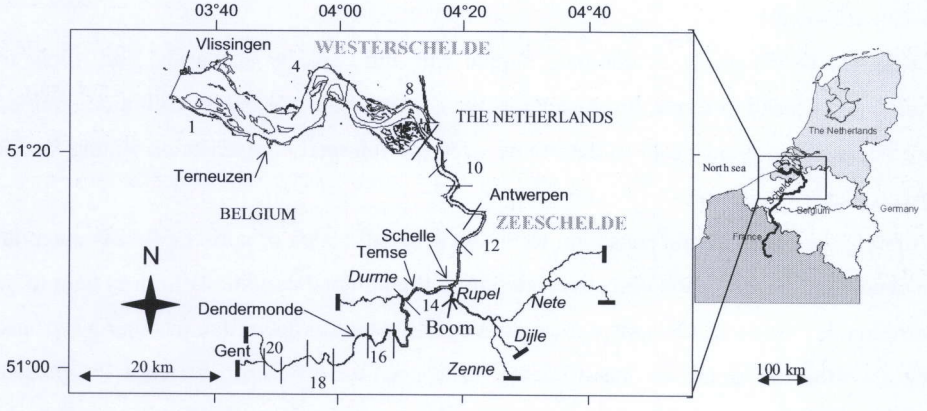


Fig. 7.1: Map of the Zeeschelde; compartments according to Soetaert & Herman (1995)

These scenarios represent average hydrological conditions, characterising a certain 'historical' state of land use and human activity. The light climate in the water column was considered equal for all scenarios, as it could not be reconstructed quantitatively.

7.2.3 Coupling with other factors

Macrofaunal biomass is related with many factors (Ysebaert *et al.*, 2005). On ecosystem scale, however, when plotted for several estuaries, a relation with primary production was found (Herman *et al.*, 1999), namely:

$$B = -1.5 + 0.105 * P \qquad (3)$$

with B in g AFDW m^{-2} and P the system averaged net primary production density (in g C m^{-2} y^{-1}).

Primary production is in turn linked with the nutrient load, as far as no other factors, such as light, are limiting. Primary production has been incorporated in many ecological models (*e.g.* Soetaert *et al.*, 1995; Hofmann *et al.*, 2008). These ecological models have the benefit that they can be used to reconstruct historic primary production scenarios of which no monitoring data are available. Equation (3) thus allows the extrapolation of historic scenario model results for water quality and primary production towards the higher trophic level of benthic macrofaunal biomass.

Equations (1) to (3) allow to compare simple carrying capacity scenarios, and allow to determine compensation terms, but as long as the scenarios are not linked with a determined quality status, there is no mean to determine what the minimal compensation should be for any given scenario to assess.

Determining the minimal compensation to obtain a 'good' status of conservation is essential in the concept of conservation objectives, requiring the minimal conditions for a system to be self sustainable. As such, the approach needs a decision tool to determine whether a scenario can be classified as 'good' or 'insufficient'. The smallest difference between the present situation scenario and any of the 'good' scenarios represents the least compensation need. As the production compensation is covered by carrying capacity equations, the decision tool is based on the qualitative requirements for conservation, *i.e.* habitat quality or species diversity. It is known that eutrophication can cause a collapse of benthic production; in anoxic systems the macrozoobenthic community will be reduced to zero. The reference for a 'good' diversity is assumed to stand also as a reference of production, as the conditions for a 'good' macrozoobenthic production are less well documented for our example, the Zeeschelde.

The present situation can so be evaluated amongst different scenarios, allowing, in case of a bad condition, a quantification of the effort that is necessary for recovery, expressed either in

terms of surface, or quality, expressed as a required biomass density increase. It is perfectly possible that an assessment of the present situation scenario could turn out to have more benthic standing stock than *e.g.* the pristine scenario, for instance if the present biomass production would be relatively higher than any corresponding loss of habitat.

The elements required for applying our presented approach are habitat area evolution, benthos biomass production evolution through modelling of primary production, the determination of the limiting factor of habitat quality or species diversity and the effect of this factor on biomass production.

7.3 Application of the conceptual approach

7.3.1 Study site: the Zeeschelde

The watershed of the river Schelde is approximately 21.863 km^2. With about ten million people or 477 inhabitants km^{-2} it is one of the most densely populated watersheds in the world. The Scheldt is a typical rain fed lowland-river, stretching over 355 km from source (St. Quentin in the north of France) to the mouth (Vlissingen). The estuary of the river Scheldt (Fig. 7.1) extends from the mouth in the North Sea at Vlissingen (km 0) till Gent (km 160), where sluices stop the tidal wave in the Upper Scheldt. The tidal wave also enters the major tributaries Rupel and Durme, providing the estuary with approximately 235 kilometres of tidal river. The Zeeschelde, the Belgian part of the Scheldt estuary (105 km long), is characterized by a single ebb/flood channel, bordered by relatively small mudflats and marshes (28% of total surface). The surface of the Zeeschelde amounts to 44 km^2. A freshwater zone (limnetic plus oligohaline) zone stretches from Gent down to about Antwerp (82 km from Gent). Between Antwerp and the Dutch Belgian border the water is mesohaline with considerable salinity changes (Van Damme *et al.*, 2005). A more detailed description of the Scheldt estuary is given in Meire *et al.* (2005). This study is restricted to the Zeeschelde. By cutting away the Dutch part of the estuary, the error of not knowing the scenario values of the sea boundary is minimized.

7.3.2 Mudflat area evolution

Although the overall loss of intertidal habitat of the Scheldt estuary is fairly well known (Meire *et al.*, 2005), no detailed information on the loss of mudflat area was available. This was reconstructed by careful analysis of several maps.

The loss of tidal flats in the Zeeschelde was reconstructed by digitising with ArcGIS 8 (ESRI) old maps and areal photographs. The oldest material is the so called Van der Malen map of 1850. The mudflat area of 1950 was determined in the same way using the map of 'Depot de la guerre' (1950). In 1990 and 2004, orthophoto's were taken from the whole Zeeschelde at low tide in order to construct vegetation maps. A digital elevation model (DEM, a combination of high tide bathymetric sonar and low tide altimetric laser data) that was made in 2001 was used to interpret and refine the results from the orthophoto's. Changes in the intertidal mudflat area through embankment, river straightening, dike construction, industrial infrastructure works, bank fortification, erosion and de-embankment were calculated for 1850, 1950, 1990 and 2004. There was no way to determine the mudflat area before 1850. For lack of better estimates, it was assumed that the mudflat area remained constant from pristine times till 1850. Between 1950 and present, missing values for time intervals were interpolated linearly. It was assumed that for the '2015' scenario, the mudflat area remained the same as the '2000' scenario, so that the compensation area of the future is set relative to the present situation.

The evolution of the total mudflat area of the Zeeschelde, including all tidal parts of the tributaries, is biased by missing information for some compartments, especially in 1990 (Table 7.1). In spite of these gaps, the trend is clear: since 1850 more than 900 ha of intertidal mudflats were lost in the Zeeschelde, corresponding with approximately only one third of the habitat available in 1850.

Between 1850 and 1950, the main loss could be attributed to land winning, from 1950 to 1990 infrastructure works and dike construction showed to be the main factors of mudflat area reduction. Since 1990, intertidal mudflats were probably mostly lost by erosion.

Table 7.1: Area evolution (ha) in the Zeeschelde and tidal tributaries; compartments according to Soetaert & Herman (1995)

Section	1850	1950	1990	2004
compartment 9	757	257	241	197
compartment 10	169	169	116	96.3
compartment 11	183	183	126	81.8
compartment 12	103	91.0	57.8	35.7
compartment 13	56.7	51.0	41.7	29.1
compartment 14	83.5	82.2	71.0	40.5
compartment 15	24.1	31.6	21.4	19.2
compartment 16	17.7	17.7		8.23
compartment 17	17.6	17.6		7.49
compartment 18	10.8	10.8		0.63
compartment 19	10,2	10.2		1.15
Dead end Melle-Gentbrugge		25.0		23.9
Durme			34.6	24.7
Rupel	38.7	38.7		26.1
Dijle-Zenne-Nete				0.31
Total	**1472**	**985**	**709**	**592**

7.3.3 Limitation of estuarine diversity

Indications that the oxygen concentration of the Zeeschelde is the prime factor that has affected its species diversity are amply available, *e.g.* the species composition of the benthic macrofauna (Seys *et al.*, 1999), the fish fauna (Maes *et al.* 2004), or the distribution pattern of the copepod *Eurythemora affinis* (Appeltans *et al.*, 2004). However, quantified oxygen demands of species or communities that belong to the Zeeschelde are scarcely documented, and estuarine oxygen standards . Although water quality standards are amply available, no standard method exists to derive oxygen concentration standards with respect to estuarine whole system diversity. Relations between oxygen are restricted to. Therefore the only way to derive such standard is by combining all individual studies that link species sensitivity or community composition with oxygen, including physiological and ecotoxicological single species studies (*e.g.* Ross *et al.*, 2001) and correlations between dissolved oxygen concentration and community composition. Arguments are listed for fish, benthos and zooplankton.

The response of fish species on increasing dissolved oxygen concentrations, expressed as the probability that a fish is caught in a fike over a 24 hour period, has been modelled by Maes *et al.* (2004). The response results can be divided into two groups: migrating species (execpt

Anguilla anguilla and *Gasturosteus aculeatus*) showed a significant response while most freshwater species or estuarine resident species showed no response (Maes *et al.*, op.cit.). Maes *et al.* (2008) modelled that a minimum oxygen concentration of 5 $mg.L^{-1}$ can restore the migration route of *Alosa fallax*. Initially an oxygen concentration, corresponding with 50% probability to catch the fish of a certain species, is proposed as criterion for a good oxygen condition for the species. But the fike catch results were obtained independently of the seasonal migration pattern. This criterium corresponds with the estuarine criteria propsed by the US Environmental Protection Agency. A correction for temperature and seasonal occurrence was therefore presented, showing a considerable differentiation for *e.g. Allosa fallax* and *Liza ramada* (Maes *et al.* in prep.). The resulting criteria for migrating species range between 1.5 mg L^{-1} for *Anguilla anguilla* to 7.5 mg L^{-1} for *Liza ramada*. As *L. ramada* is considered to be typical for coastal zones and estuaries, migration of this species to the fresh water zone would be rather elective, so that the high criterion for this species can be questioned. The other criteria correspond well with criteria for comparable American species, *e.g.* 5 mg L^{-1} for Alosa sapidissima (Stier & Crance 1985) and 6 mg L^{-1} for several Osmeridae (Dean & Richardson, 1999). Although juvenile fish is generally more sensitive to oxygen than adults, they are capable of avoiding oxygen poor conditions (Wannamaker & Rice, 2000; Richardson *et al.*, 2001), or show physiologic adaptations to withstand hypoxia during short periods (Ross *et al.*, 2001).

In 1964, before a long period of severe deterioration of the water quality, a very diverse macrozoobenthos community was found in the freshwater tidal area of the Biesbosch (the Netherlands), with Shannon Wiener indices between 1 and 2, at oxygen summer concentrations between 50 and 70 % saturation (Wolff, 1973). In the impacted fresh water zone of the Scheldt estuary such diversity was never recorded while recorded oxygen summer conditions only very recently amounted up to such levels of saturation.

In the oligohaline intertidal zone of the Elbe estuary, the presence of 68 macrozoobenthic species could be linked with dissolved oxygen concentrations between 5 and 6 $mg.L^{-1}$ (Krieg, 2005).

The zooplankton species *Eurythemora affinis* shifted from the brackish to the freshwater zone of the Scheldt when dissolved oxygen concentrations increased from around 1 to around 3 $mg.L^{-1}$ (Appeltans *et al.*, 2003.

Based on all previous arguments, taking into account species specific tolerance levels, migration periods and swimming capacities, and community diversity related to oxygen concentrations, it is proposed to put forward an oxygen concentration of 6 mg L^{-1} (= 187 µmol L^{-1}) between November 1st and April 30th and a weekly average of 5 mg L^{-1} (= 156 µmol L^{-1}) for the corresponding summer half year.

In case oxygen concentrations would increase in the Scheldt, other diversity limiting factors should be assessed. For instance, physical disturbance has explained diversity reduction of benthos in soft bottom sediments of the brackish part of the estuary (Ysebaert *et al.* 2000).

7.3.4 Reconstruction of historic estuarine primary production and benthic macrofauna biomass

The **RIVERSTRAHLER model** has been used to model immissions from the watershed into the Zeeschelde. It is a simplified model of the biogeochemical functioning of river systems at the basin scale allowing to relate water quality and nutrient fluxes to anthropogenic activity in the watershed (*e.g.* Billen *et al.*, 1994). The model has recently been applied to the Scheldt river system (Billen *et al.*, 2005), thus reconstructing the respective role of hydrology and human activity in the watershed during the last 50 years.

The RIVERSTRAHLER model has been applied to the upper Scheldt watershed (including the Dender river) on the one hand, to the Rupel watershed on the other hand (Fig. 7.2). The flux results represent integrated values of the fluxes discharged at Temse and Boom respectively. Because hydraulic regulation of the Leie river in the region of Ghent entirely discarded its flow from the lower Scheldt course over different canals, the Leie basin is not included in the analysis. Based on the analysis of the long term rainfall data for the Scheldt watershed over the last 50 years, the following conditions were chosen as representative of 3 classes of hydraulicity:

1995 (804 mm y^{-1}) for the 'mean' conditions, *i.e.* a mean discharge of 185 m^3 s^{-1} at Schelle
1984 (1275 mm y^{-1}) for the 'wet' conditions, *i.e.* a mean discharge of 250 m^3 s^{-1} at Schelle
1976 (541 mm y^{-1}) for the 'dry' conditions, *i.e.* a mean discharge of 65 m^3 s^{-1} at Schelle

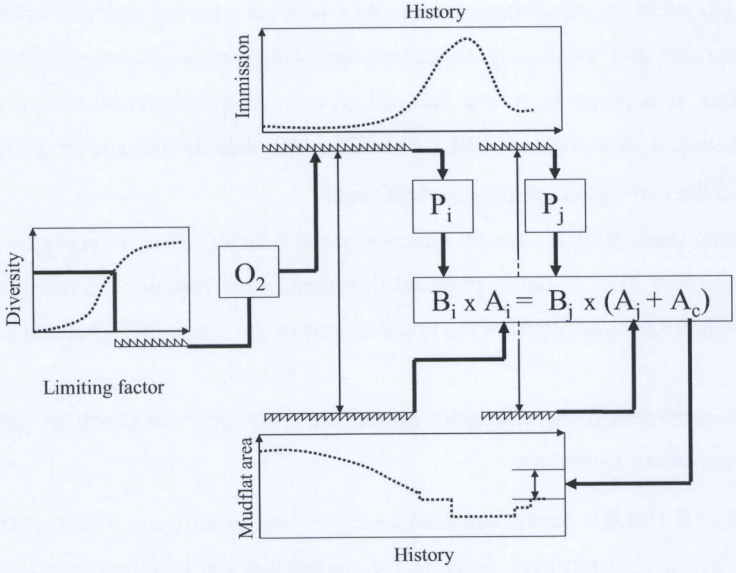


Fig. 7.2: Scheme of the scenario comparison approach. B = Macrofaunal benthic biomass production, A = area, P = primary production, i = reference scenario, j = scenario to be assessed, c = compensation

The estuarine **MOSES model** is a simplified simulation box compartment model using fixed dispersion coefficients, allowing to predict chemical and biological alterations that can take place in dissolved substances that reside in the estuary. The model is described in Soetaert & Herman (1995 a, 1995 b & 1995 c), and has since then been improved by recalibrating on data of 1980-2002, implementing the lateral input of tributaries in a better way, and reformulating the transport in the upper compartments (Cox *et al.*, in prep.).

The Riverstrahler results for the different scenarios have been used as input for the improved MOSES model. In that way the effect of specific estuarine processes could be reconstructed for the present and historical immission scenarios. The MOSES model was run on scenarios with average hydraulicity. The model results of the present '2000' scenario were, according to Hofmann *et al.* (2008), calibrated on data of 2001, a year with a mean discharge of 191 $m^3 s^{-1}$ at Schelle.

The RIVERSTRAHLER and improved MOSES models have been coupled for 4 scenarios: 'pristine', '1950', '2000' and '2015'. System averaged scenario values were averaged over the model compartments (Soetaert *et al.*, 1995), weighed for compartment volume or surface as required per parameter.

The results from the RIVERSTRAHLER model showed that the immission from the watershed has known an increase of human impact from pristine times up till the eighties

(Fig. 7.3). Detritic carbon and phosphorous show the same pattern, reflecting maximal immissions in the period 1970-1980, when the estuarine water quality was indeed bad (Van Damme *et al.*, 2005). In the nineties a period of recovery started. The limits of the progress, as set by policy makers, are marked by the future '2015' scenario. This scenario shows drastic improvement: both carbon and phosphorous immissions become smaller than the '1950' scenario and are nearing the pristine scenario. For the immission of total nitrogen, dominated by nitrate, this is, however, not the case; its immission in the estuary steadily increases, even when carbon and phosphorous loads are decreasing. The future '2015' scenario showed maximal nitrate immissions of history. A more detailed presentation and analysis of the results is given in Billen *et al.* (2005).

Using the RIVERSTRAHLER results as input in the MOSES model gave satisfactory results: The '2000' scenario of the MOSES model results show that the modelled oxygen concentrations fitted well the observed data (Fig. 7.4). The reconstructed oxygen concentrations reached our diversity standard of 156 μmol L^{-1} in the 'pristine' and the '1950' scenario (Fig. 7.4). In the '1950' scenario the summer standard was not met only in July in the most upstream compartment of the Zeeschelde. In the '2000' and '2015' scenarios, summer concentrations dropped below 100 μmol L^{-1}, and winter concentrations in these scenarios dropped below 150 μmol L^{-1} during five consecutive months. According to the European Water Framework Directive (2000/60/EG), the 'pristine' scenario corresponds to the 'very good' status for water quality. The '1950' scenario meets the requirements for good diversity, and can thus be put forward as a 'good' status scenario. Both scenarios can thus be used as a reference to assess the present situation. The '2000' and '2015' scenarios are scenarios to be assessed relative to the reference scenarios.

The primary production results showed another ranking of scenarios than the oxygen results. The production in the '2015' scenario dropped below the production in the '1950' scenario, indicating that implementation of the European Directives will resort a strong effect (Fig. 7.5). In the upstream part of the Zeeschelde , the 'pristine' and '2015' scenarios have production rates about half as big as in the '1950' and '2000' scenarios. In all scenarios primary production dropped to almost zero in the most downstream brackish compartments, which are characterised by strongly varying salinity values (Van Damme *et al.*, 2005).

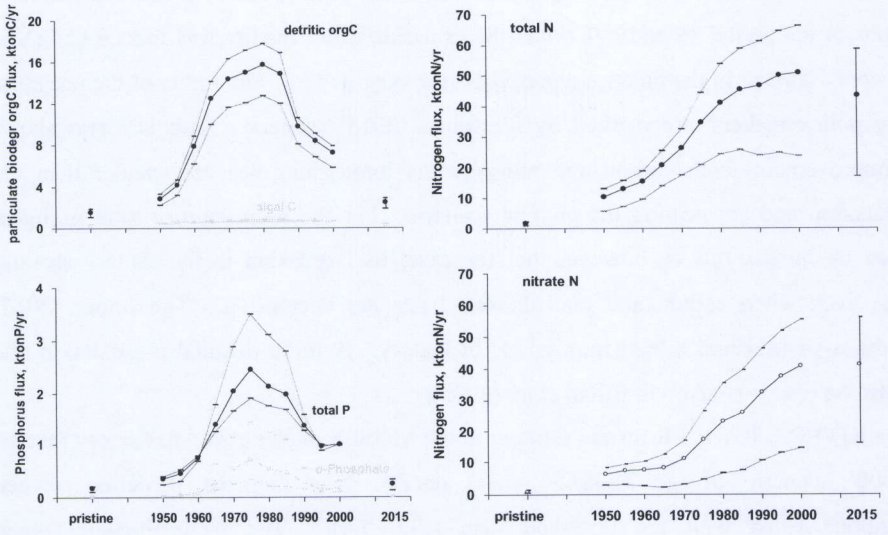


Fig. 7.3: Immissions in the Zeeschelde, as calculated with the Riverstrahler model for different scenarios

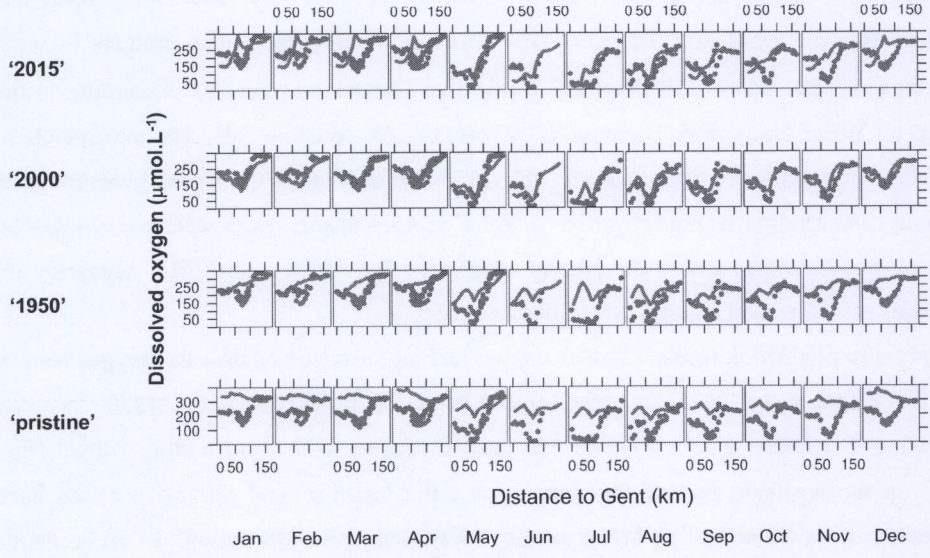


Fig. 7.4: Dissolved oxygen concentrations in the Zeeschelde, as calculated with the MOSES model for every month of 4 scenarios. Solid lines are modeled results, dots are measured data of 2001.

System averaged scenario values were highest for the '2000' scenario, 55.4 g C m^{-2} y^{-1} and lowest for the 'pristine' scenario, 19.1 g C m^{-2} y^{-1} (Table 7.2). The corresponding chlorophyll a concentrations showed a similar pattern as primary production (Fig. 7.5). Concurrent with

the immission values of total nitrogen and nitrate (Fig. 7.3) the concentrations of total dissolved inorganic nitrogen (TDIN) and nitrate were almost equal for the '2000' and '2015' scenarios (Fig. 7.5). High rates of nitrification in the Zeeschelde (Vanderborght *et al.*, 2002 ; Hofmann *et al.*, 2008) are explaining the low oxygen concentrations for the '2015' scenario. The system averaged macrozoobenthic production, as calculated from the system averaged primary production (Table 7.2) with equation (3) amounts from 2.6 % ('pristine' scenario) to 7.7 % ('2000') of the system averaged primary production.

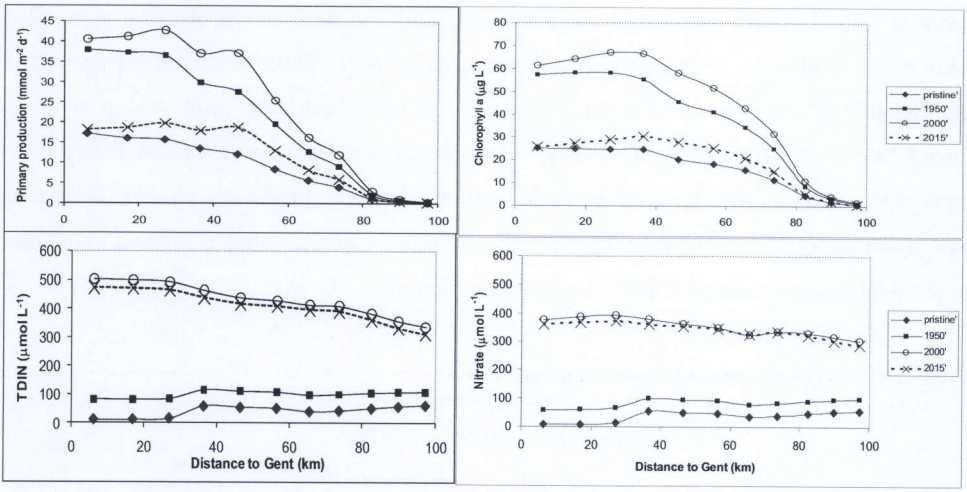


Fig. 7.5: Primary production, chlorophyll a, total dissolved inorganic nitrogen (TDIN) and nitrate in the Zeeschelde, as calculated with the MOSES model for 4 scenarios

Table 7.2: Values used for scenario comparisons

Parameter		'pristine'	'1950'	'2000'	'2015'
System averaged primary production	(g C m^{-2} y^{-1})	19,1	43,6	55,4	27,3
System averaged benthos production	(g AFDW m^{-2} y^{-1})	0,5	3,1	4,3	1,4
Total system mudflat area	(ha)	1472	985	592	?

7.3.5 Mudflat area assessment

Using the reconstructed system averaged macrozoobenthic production and area evolution (Table 7.2), area needs were calculated with equation (2) for the '2000' and '2015' scenarios,

with the 'pristine' and the '1950' scenario as reference (Table 7.3). If the '1950' scenario is used as reference, then the compensation demands amount to 111 hectares of mudflats for the present situation, or to 1635 ha when the improved water quality allows a primary production of only half that of the '2000' scenario (Table 7.3). When the 'pristine' scenario is used as reference, the '2000' and '2015' scenarios offer enough carrying capacity for benthos, as the area needs are negative. The habitat area of the pristine scenario was set equal to the oldest documented habitat area, which is of 1850. If the pristine habitat area would turn out to be at least 125 ha larger than in 1850, then the area demand for the '2015' scenario would become positive, and it would become positive for the '2000' scenario if the pristine area would amount up to 5000 ha. It is known that between 1650 and 1800 the intertidal storage area of the Scheldt estuary decreased with 99 km^2, of which about one third was part of the Zeeschelde (Van der Spek *et al.*, 1997). The ratio of marshes vs mudflats of these former areas is not known. On the other hand, in pristine times, the freshwater zone of the estuary was probably a non tidal riverine stretch. To avoid these uncertainties it is more convenient to use the better documented '1950' scenario as reference.

Table 7.3: Area compensations between scenarios (in ha)

Reference	'2000'	'2015'
'1950'	111	1635
'pristine'	-420	-47

7.3.6 Validation

This paper presents a method to quantify the estuarine mudflat area demand corresponding with a good state of conservation combined with conditions for a good ecological status. The method relies on a comparison of carrying capacity scenarios, and on a trophic relation between primary production and macrofaunal biomass production. Such a direct relationship between primary production and carrying capacity for higher trophic levels has been identified for several ecosytems. In pelagic systems such relations even matched on species level: herring populations were related with primary production although they feed on zooplankton as intermediate trophic level (Perry & Schweigert, 2008). For benthic communities the relation might be more biased. A validation of the results is therefore essential.

The presented approach to determine mudflat area budgets relies mainly on modeled results, on the relation between primary production and macrozoobenthos and on the soundness of the conceptual approach in general.

Model validation of both Riverstrahler (Billen *et al.*, 2005) and MOSES models (Soetaert *et al.*, 1996) has proven satisfactory, but this validation refers to the '2000' scenario only, with data of 2001 (*e.g.* Fig. 7.4). As illustrated before (Fig. 7.5) the water quality of the Scheldt estuary is actually changing. A regime shift has taken place in 2004, leading to higher oxygen concentrations, even supersaturation levels in the freshwater zone (Cox *et al.*, 2009). At decreasing nutrient concentrations an increase of chlorophyll a concentrations was noted. A possible factor could be the end of ammonia intoxication with decreasing ammonium levels. The regime shift has two implications. First, it is expected that oxygen will cease to be the limiting factor for diversity. Van Eck *et al.* (1993) predicted that a recovered oxygen status might trigger a massive dissolution of heavy metals. Preliminary calculations indicate that it is not certain if heavy metals will take over the role as diversity limiting element (Teuchies *et al.*, in prep). It is not even known if the next limitation on diversity is chemical or physical or anything else. Our approach remains applicable at changing diversity limitations as far as they are quantified. Second, regime shift behaviour of primary production is, admitted, not incorporated in the used models. Many factors were considered constant between scenarios, such as estuarine and riverine morphology and light climate. In the Scheldt estuary light is more limiting for primary production than nutrients (Soetaert *et al.*, 1995b), but reconstructing changes among scenarios lead no further than a semi-quantitative estimate that suspended matter concentrations were about a quarter to one third less before the embankments in the Scheldt estuary between 1650 and present (Van Damme *et al.*, 2009).

The interestuarine trophic relation between primary production and benthic macrofaunal production that was used in this study (equation 3), was based on data of the Scheldt estuary, but only of the polyhaline and mesohaline zone (Herman *et al.*, 1999). The Zeeschelde was considered as being one ecosystem, despite the different characteristics of both primary production and benthic macrofauna along the salinity gradient. In order to assess the validity of the trophic relation and to validate the modelled results, data of primary production and macrobenthic fauna need to be compared taking into account the salinity gradient. In the mesohaline part of the Zeeschelde primary production decreases with increasing salinity from the values in the freshwater zone to zero or negative values in the mesohaline zone (Kromkamp & Peene, 1995; Kromkamp *et al.*, 2005), as the phytoplankton communities

showed strongest changes in species composition and decrease in biomass of both marine and freshwater populations between 0.5 and 5 psu salinity (Muylaert *et al.*, 2005). An overview of primary production data in the freshwater part of the Zeeschelde and other estuaries is given by Van Damme *et al.* (2009). The primary production in the freshwater zone of the '2000' scenario ranged between 162 to 193 g C m^{-2} y^{-1}. This is in the range of primary production rates of 108 (Muylaert *et al.*, 2005), over 388 (Kromkamp & Peene, 1995) to 500 g C m^{-2} y^{-1} (Kromkamp *et al.*, 2005). The modeled primary production values of the '2000' scenario were thus in agreement with other data.

The changes of diversity and species composition of the soft-sediment benthic macrofauna along the salinity gradient of the Scheldt estuary have been described by Ysebaert *et al.* (1993; 2003). The average biomass in the mesohaline part of the estuary was in the subtidal zone 0.94 g AFDW m^{-2} (Ysebaert *et al.*, 2000) and in the intertidal zone 6.7 g AFDW m^{-2} (Ysebaert *et al.*, 2005). In the oligohaline part of the estuary a sharp decrease in species richness and biomass was observed. In the freshwater tidal part of the Zeeschelde the benthic macrofauna of soft sediments is mainly constituted of Oligochaeta (Ysebaert *et al.*, 1993; Seys *et al.*, 1997). The presence of this impoverished benthic fauna was mainly caused by the bad water and sediment quality of this part of the estuary. The average biomass in the intertidal zone varied between 3.8 g AFDW m^{-2} in 1996 and 1.7 g AFDW m^{-2} in 2002. For the subtidal zone only sufficient data are available for 1996, showing an average biomass of 1.6 g AFDW m^{-2}. For the whole freshwater tidal zone of the Zeeschelde we estimated the average biomass at 2.5 g AFDW m^{-2}. For the Westerschelde, the system averaged biomass was estimated at 10 g AFDW.m^{-2} (Herman *et al.*, 1999).

Summarizing for the whole Zeeschelde we estimated the average yearly total benthic biomass at 3.1 g AFDW m^{-2}. Based on a weighted average, considering the relative surface of the intertidal and subtidal zone, a rough estimate of 1.7 g AFDW m^{-2} is obtained for the whole Zeeschelde. It can be concluded that equation (3) can be called representative for the Zeeschelde as a system. This is not evident, as the relation might be biased by some factors, as the evolution of light limitation as metioned earlier. In the freshwater part the anthropogenic fraction of the particulate organic carbon has been estimated at around 45% during summer and 80% during winter (Hellings *et al.*, 1999; Van Damme *et al.*, 2005). The dominant benthic group in the freshwater and oligohaline part of the Zeeschelde consists of Oligochaetes, which are detrivores. Apparently, the biomass increase due to consumption of antropogenic detritus was not larger than the error margins of the approach. The reduced

residence time of the water in discharge dominated sections, and hence a restriction of plankton availability for benthos, could also alter the relation for the fresh water zone.
Despite the inevitable knowledge gaps, the approach is sound enough as a best possible estimate to derive conservation objectives for estuarine management.

7.3.7 Management

At first sight the results are ambiguous for estuarine managers. Depending on the choice of reference scenario, compensations can either be positive or negative. Even when the option for the better documented '1950' scenario as reference is made, compensation areas differ an order of magnitude if the '2000' or '2015' scenarios are assessed (Table 7.3). The immissions of the '2015' scenario are, however, close to the '1950' scenario, as only the nitrogen immissions need to be reduced (Table 7.4). In contrast with the modelled results, however, the trend of TDIN in the Zeeschelde has been decreasing since the eighties (Soetaert *et al.*, 2006) and this trend persisted also during the last decade (Fig. 7.6). At the downstream boundary of the Zeeschelde (93 km from Gent) the decrease was 16% during the last decade, while in the freshwater and oligohaline zone (km 0 - 52 from Gent) the decrease was about 33%.

Table 7.4: Reduction of immission (in %) required to meet the immissions of the '1950' scenario, for a wet, dry and mean year (BPOC = particulate biodegradable organic carbon, DOC = dissolved organic carbon)

	'2000' scenario			'2015' scenario		
	dry year	mean year	wet year	dry year	mean year	wet year
BPOC	61	60	58	0	0	0
DOC	38	34	34	0	0	0
NH_4^+-N	71	60	58	0	0	0
NO_3^--N	81	84	85	83	84	85
N tot	76	79	80	67	76	78
PO_4^{3+}-P	89	85	81	0	0	0
P tot	77	65	60	0	0	0

Adding mudflat area to the system has a positive feedback on reducing the nitrogen load through benthic denitrification. Taking into account Middelburg *et al.* (1996) and Van Damme *et al.* (this work, chapter 5), a system averaged denitrification rate of 10 mol m^{-2} y^{-1} is acceptable, leading to the result that adding 1635 ha in the '2015' scenario would reduce the

immited nitrogen load with 5.6 %. This is not enough to reach the required 84 % reduction (Table 7.4), but together with the observed TDIN reduction over the last decade, the goal for '2015' is about half met. Recalculating the '2015' scenario taking into account the observed reduction yields an area compensation result of 785 ha. If this decrease would persist up till 2015, then an area claim of around 500 ha would be sufficient to compensate for loss of macrozoobenthic stock since '1950'. This claim of 500 ha is presented as a management target, on the condition that this area must be suitable for macrofaunal benthos, but also for the wader birds that feed on them. Additional mitigation measures and initiatives are needed, such as avoidance of disturbance, spatial area distribution, deriving an optimal slope for mudflat habitat, taking into account foraging density by birds, etc.

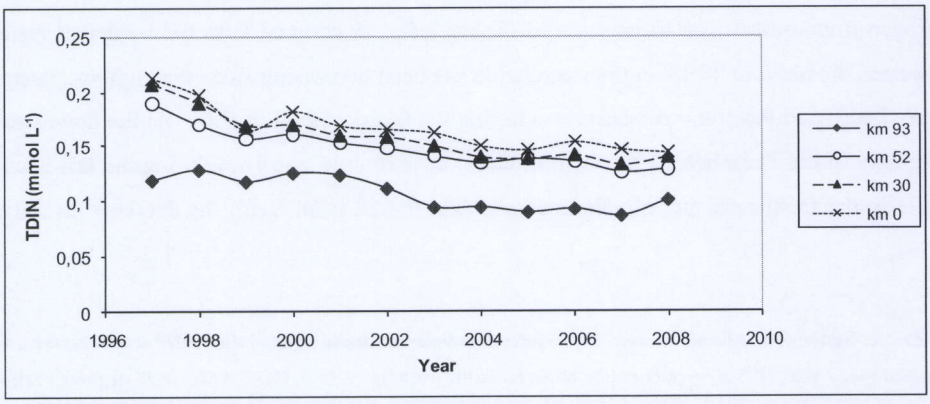


Fig. 7.6: Concentrations of total dissolved inorganic nitrogen (TDIN) over the past decade at 4 locations the Zeeschelde

7.4 Conclusions

A method to assess the need of mudflat habitat area has been presented, and was applied on the Zeeschelde, leading to a quantified area claim for benthic macrofauna as food for birds and fish. The Zeeschelde proved to be a complex case, due to the presence of both a brackish and a fresh water tidal zone of which the hydrology is partly dominated by discharge events. The concept will be easier applicable on more saline transitional waters. Nevertheless, the approach could be validated. The role of water quality, primary production and species diversity has been quantified, but other factors linked with system dynamics, morphology and specific habitat also need to be taken into account. If all these required data are covered, then

the integration of datasets through this method could offer a strong universal tool to assess habitat need in a wide array of estuarine systems, as the method is based on fundamental trophic relationships. The benefit of this approach is situated in the combined implementation of both the European Habitat - and Water Framework Directives, as reference conditions and quantifications of good ecological state conditions were incorporated in the quantification of a good state of conservation of priority habitat. The approach might in other perspectives also be applied on the more open coastal systems, *e.g.* to check if benthic biomasses have been suppressed by human impacts.

Acknowledgements

This research was funded by the Flemisch Administration for Waterways and Maritime Affairs, division Zeeschelde. We thank the Fund for Scientific Research for funding the Scientific Community 'Ecological characterization of European estuaries, with emphasis on the Schelde estuary' (project nr. W 10/5 - CVW.D 13.816), and for funding Dutch-Flemish ecological research projects on the Schelde (project nr. G.0439.02).

Chapter 8

Synthesis

Van Damme S.

This study is exceptional in the way that it took almost 15 years from the first measurement in December 1995 to the eventual submission of the thesis in 2010. The advantage is that a spectacular system evolution has been witnessed throughout the progress of the work.

The knowledge of estuarine systems and freshwater tidal areas in particular has evolved from bits and pieces to more thorough insights. Policy and management have followed a long track. Fifteen years ago, the Zeeschelde was a transitional system also from a policy point of view. It was a gate between sea, ports and hinterland and a zone of hazard between the restless waves and the peaceful land. Most measurements were done in this respect. Monitoring of water quality and ecology of the Zeeschelde was largely fragmented in time and space, and was passed on over different institutions. The ecological functioning was not understood and was no subject of integrated management.

This picture has changed. The Zeeschelde has gained a reputation of integrating safety, accessibility and ecology. The performed work had the essential aim to contribute to the revalorisation of the Zeeschelde. It is up to others to judge if it did.

8.1 Monitoring

In December 1995 the OMES program was launched in order to fill up the many gaps of knowledge that prevented fundamental ecological management. At that time there was still uncertainty on the typology of the Zeeschelde. Estuaries can be defined according to the salinity gradient or according to the tidal influence. For the Zeeschelde, the difference between the two typology implementations has serious consequences towards management, as the freshwater tidal zone (including the oligohaline zone) extends for about half of the length of the Schelde estuary (**Chapter 3**).

The central target of the OMES scientific program was the extension of an ecosystem model. During 7 years, monitoring of water quality parameters was performed covering the entire Zeeschelde. For the first time a coherent view of the water quality from the river mouth at Vlissingen to the most upward boundary in Gent was presented, integrating the results of several partners. It can be considered as a statement that an estuary does not end at the interface between brackish and fresh water, but that it extends inland as far as the tidal influence reaches. To confirm this statement however, functional evidence was needed. Apart from a view on spatial and interannual variability (**Chapter 3**), linking the results of the different partners offered functional insights. A major finding was that the energetic zonation of the freshwater part of the Schelde (Chen *et al.*, 2005) was characterised by separate fytoplankton communities (Muylaert *et al.*, 2000) (**Chapter 2**). This finding served as a helpful argument to accentuate that the freshwater part of the Zeeschelde was not to be regarded as a riverine system, but that it could be divided into a truly estuarine freshwater zone with estuarine species occurring in a tide-dominated part, and a discharge dominated zone where riverine species are imported from the river. Up till today, policy has stuck to the salinity option in defining the Schelde estuary, which is in a strict sense in agreement with the Water Framework Directive (WFD). However, it is a wrong decision, showing a weakness in the directive. Estuarine managers face WFD implementation problems with the current administrative zonation of the estuary. Basing the administrative zonation on estuarine functioning rather than on responsibility affinities will overcome this problem.

Learning from monitoring results requires more than just an overview of the concentration data. The observed concentrations are a result of different processes (**Chapter 4**). Precipitation flushes the catchment through erosion, run off, leaching, flushing of sewage systems and water treatment plants, etc. Enhanced river discharge flushes not only the catchment but also the estuary, so that the time span of estuarine organisms to interfere with biogeochemical cycles is shortened. Concomitant, the loads are diluted by the accumulated water masses. This study showed that each of these regulators interacts substantially with water quality parameters such as nitrogen and dissolved silica. For other parameters, unravelling the mechanisms remains unapplied. For instance, although a general insight is available, the influence of dilution and changes of residence time on gas emissions (**Chapter 5**) from the Schelde is not documented from field data, although it was clear from our comparison that gas emission from the pelagic compartment is more important than from intertidal sediments.

Linking the data of the Zeeschelde and Westerschelde triggered a long term trend analysis covering the full salinity gradient (Soetaert *et al.*, 2006). Extrapolation of the trends proved to be tricky. Unexpected drastic changes have recently occurred that had characteristics of a regime shift and that were unpredicted by the existing models (Cox *et al.*, 2009). It stressed the need for smart monitoring, complemented with a thorough analysis. The need for monitoring has been understood by estuarine managers. The legal framework that urges for monitoring contains many laws and rules. The obligations reach out far, deep and encompassing, but are not specified at all with exception of the WFD. To cover all needs and to comprehend the functioning of the system, its changes and the effects of management tools, it was agreed to merge the separate monitoring efforts into a transnational integrated strategic monitoring program, wiping off overlaps and filling gaps where needed. The expertise that was built up during this study helped in reaching a cost efficient omnivalent monitoring program for the Schelde estuary.

8.2 Ecological functions of tidal marshes and mudflats

Management of dynamic systems would turn out problematic if a static approach is maintained. Estuarine habitats evolve constantly towards moving equilibria. A

functional approach overcomes such structural changes and is therefore more appropriate than pinning down stern habitat limits that eventually will come into friction with a latter system equilibrium shift.

Although many ecological functions can be listed, an exhaustive overview of estuarine functions has not been made so far. Examples include the buffering of tidal energy, water storage capacity, spawning grounds, water aeration, etcetera. In this thesis, only the functions related to water quality were adressed, although not to be neglecting links with other fields have on several occasions been added.

Of all biogeochemical aspects studied in this work, the ecological function of freshwater tidal marshes exhibiting the largest effect was oxygenation of the incoming estuarine water. This is remarkable as marsh sediments are known to consume oxygen (Eriksson *et al.*, 2009). In tidal marshes adjacent to unaffected estuaries the aeration function stays latently hidden. As the oxygen concentration of the estuarine water is affected, the marshes are capable of providing local refuge zones for aquatic fauna.

The important release of DSi from freshwater tidal marshes was an unexpected new finding. This work triggered detailed research on silica cycling in tidal marshes. Tidal freshwater marshes are now known to recycle biogenic silica (BSi) to dissolved silica (DSi). They store large amounts of BSi in vegetation and sediments. BSi is easily soluble if compared to lithogenic Si. Dissolution of BSi results in pore water concentrations that can be more than 7 times higher than the pelagic concentration of DSi in summer. Fed by both a small but rapidly recycled sink for Si in vegetation and a large but slowly recycled sink for Si in sediment, the pore water enrichment is entrained by inundation water (Struyf *et al.*, 2005b; Struyf *et al.*, 2007). This explains the control of the seepage water on DSi export in the observed freshwater tidal marshes.

Nitrogen removal was observed in a freshwater tidal marsh (**Chapter 6**) and in mudflats along the longitudinal and vertical gradient (**Chapter 5**). The nitrate removal rate in the mudflat of Appels and the Tielrode tidal marsh were of the same order of magnitude (between 1 and 2 $mmol.m^{-2}.d^{-1}$). In the mudflat of the Durme tributary 4 times higher values were found, while on average less than 1 $mmol.m^{-2}.d^{-1}$ was observed in the most saline mudflat. Denitrification rates were intense, although the effect on the nitrogen load passing through the estuary was very limited.

Eventually, not only the loads but also the nutrient ratios determine eutrophication in estuarine and coastal waters. In the freshwater tidal marsh, import of inorganic N and export of dissolved Si contributed about equally against non diatom algal blooms. This work (**Chapter 6**) was a precursor for a system covering isotope study in the same tidal marsh (Gribsholt *et al.*, 2005; 2006). Denitrification was in this study not directly measured and could potentially be maximum 15 % of the experimentally added nitrogen, probably less. We found higher values of recovery. While in the marsh the silica cycle is now better known than the specific denitrification rates, the situation in the mudflats is reverse. On top of local nitrate production by benthic nitrification, denitrification in the mudflats showed to be fed and limited by the nitrate supply from flooding water. As such, it is likely that denitrification in mudflats is more intense than in the adjacent marshes of the Zeeschelde. Moreover, recent monitoring shows that the restored oxygen concentrations in the estuary are related with a gradual decrease of ammonium and a concommittant increase of nitrate (Maris, written comm.). The denitrification rates in the mudflats are expected to increase.
The silica picture is quite different. The dissolved silica release from marshes is fed in large extent by a small but reactive vegetation Si stock. The Si cycle in mudflats is less known, but surely the vegetation stock of the marshes can on the mudflat only be represented by microfytobenthic mats. Even if this algal stock is recycled faster than the marsh vegetation, it is hard to assume that fytobenthic mats can rival with the Si rich Phragmites plants in DSi release. Asmus *et al.* (2000) documented both net import and export of DSi in intertidal sites with microfytobenthos according to specific conditions. Concluding we hypothesise that both marshes and mudflats might contribute equally to shift the pelagic N/Si ratio away from non diatom blooms, but that they both do so with different relative contributions for N and Si (Fig. 8.1). To test this hypothesis further knowledge is needed on the denitrification process in marshes and on silica cycling in mudflats.

8.3 Functional restoration

The onset of this thesis was the former reputation of the Schelde estuary of being an open sewer. Carbon and phosphorous loads could be reduced with enhancing water treatment. Nitrogen however and especially the diffuse pathways of nitrate needed

other solutions. Riparian buffer strips to intercept nitrate from groundwater flows are a prime management option along the full river stretch. As the tidal marsh level is most often situated above the adjacent polder land, the buffer strip function is thought to fail in estuaries. The estuary however offered a more interesting win win solution. The area and quality of intertidal habitats have progressively degraded by land winning, deepening the waterway and other morphological changes. Using the tide as a transport mechanism to supply denitrification with nitrogen as well as creating the necessary alternating oxydating-anoxic conditions, the nitrogen removal function was a possible argument to promote restoration of intertidal habitat. This argument stands. Denitrification in intertidal areas is highly variable but has on average high values compared to other systems. The concomittant emission of the N_2O greenhouse gas is of minor importance compared with emission of CO_2 and methane (**Chapter 5**).

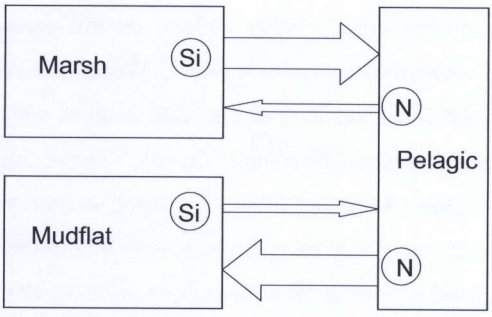


Fig. 8.1: Conceptual net N and dissolved Si fluxes between estuarine compartments

Some arguments have appeared to widen the focus from nitrogen. The nutrient limitation of eutrophication has shifted (Billen *et al.*, 2005). And from the management of safety against floods a major opportunity arose.

After a major flooding in 1977 the Belgian government initiated the 'Sigma plan' to protect the Flemish part of the Schelde estuary from tidal surges. Hydrological models predicted that, if no measures were taken, the return period of high tide topping over the dikes would increase as a result of sea level rise and deepening of the navigation channel. The flood risk would increase from an already unsatisfactory return period of once every 369 years to once every 72 years in 2050 and to once every 23 years in 2100.

The actualisation of the Sigmaplan offered three options:

- Heightening and strenghtening the dikes
- Installing flood control areas (FCA's)
- Constructing a storm surge barrier

The data gathered during this thesis were used to extend an existing ecological model over the complete fresh water tidal area of the Schelde estuary. One application of this model was to support the economic quantification of aeration and denitrification in the cost benefit analysis of the Sigmaplan actualisation options. The economic value of the ecological functions was a decisive factor in favor of flood control areas. Ecosystem functions translated into human benefit are called ecosystem goods or ecosystem services (Fisher *et al.*, 2009). Flood control areas however give the opportunity to install estuarine ecosystem services. When there is no risk of flooding, the storage volume of the flooding area can be used to allow water to enter and leave the area through a sluice system, according to the tide. The position and design of the sluices determine the rate and timing of water coming in and out. In this way, the tidal amplitude in an indation area can be tuned according to the services or habitats that are preferred. Flood control areas with such controlled reduced tidal regimes are called FCA-CRT's. One pilot CRT (Lippenbroek) serves as a scientific monitoring ground to assess the ecosystem service delivery. The results of this thesis (**Chapter 6**) were used to make comparisons between tidal marshes and CRT marshes. For instance, silica balances in the CRT habitats confirmed the high summer export results of the Tielrode marsh (Jacobs *et al.*, 2008).

Management plans and stakeholder interaction required well-founded quantified habitat needs to determine the zoning of flood area implementation. In **Chapter 7** is explained how this was done based on the existing knowledge (including **Chapter 2** and **Chapter 3**). The outcome of **Chapter 7** has been edicted by decree in stating a rehabilitation plan requiring the mudflat area that was quantified in this thesis. In the future, new knowledge will certainly have effect on the quantification. Especially the incorporation of morphological and hydrological knowledge is needed to obtain better insights in the evolution of the suspended matter concentrations and the light climate

of the estuary. An intercalibration of the method is needed with other methods as well as with other systems.

The quantification of a required mudflat area based on production and diversity aspects however covers but one single question concerning ecological service delivery. Many other functions are waiting to be assessed for service delivery.

Whereas now it is not even possible to haver a proper list of estuarine functions, goods and services, ultimately it is the aim to be able to assess all quantified ecosystem goods and services so that policy makers can base future prospectives on an equally balanced appreciation of needs for safety, accessibility and ecology. The true ambition of this thesis was to illustrate that the complexity of the fields of ecology can be overcome to make this possible.

Chapter 9

Nederlandstalige samenvatting

Van Damme S.

Estuaria zijn, als overgangszones tussen het zoete water van het land en het zoute water van de zee, bijzondere gebieden. Veel belangrijke havensteden zijn ooit ontstaan in de beschutting van estuaria, op het meest inlandse punt dat vanuit zee door schepen kon worden bereikt. Als knooppunten van handel, bedrijvigheid en welvaart zijn ze niet meer weg te denken uit de economische geografie. Ook op ecologisch vlak bekleden estuaria een bijzondere status. Ze zijn onmisbaar voor de trekroutes van talrijke vogel- en vissoorten, ze dienen als kraamkamer voor o.a. garnalen en vis, en herbergen in hun unieke habitats tal van soorten. Estuaria worden gekenmerkt door een overgang van zout naar zoet water, door een verhoogde graad van troebelheid, en door het feit dat voedingsstoffen, plantaardig afbraak materiaal en andere stoffen erin terecht komen vanuit het hele aansluitende rivierbekken. Daardoor zijn estuaria van nature zeer productieve systemen.

Door de menselijke bedrijvigheid die de omgeving van estuaria meestal karakteriseert zijn een aantal typische problemen ontstaan. Inpolderingen en uitdiepingen hebben de stromingen doen toenemen en het areaal aan natuurlijke habitats doen slinken. De vuilvracht is toegenomen en leidde, in het geval van de Schelde, tot quasi zuurstofloos water in de jaren '70 en '80. Waterzuivering kan soelaas brengen voor het aandeel koolstof en fosfor van de vuilbracht. Stikstof daarentegen beweegt onder de vorm van nitraat mee met het grondwater, ontsnapt voor een groot deel aan waterzuivering en duikt dan op in watersystemen waar het tot ongewenste algenbloei kan leiden. Denitrificatie is een specifiek proces dat nitraat omzet tot atmosferische stikstof. Stimulansen voor denitrificatie zijn de aanwezigheid van een koolstofbron en zuurstofarme condities. Zuurstofrijke condities zijn dan weer goed om

ammoniumstikstof om te zetten naar nitraat. Kortom, getijdenwerking wordt als een potentieel belangrijke factor en als laatste kans beschouwd om stikstof uit het water op te ruimen voor het de kustwateren bereikt.

Doel van dit werk was om de rol van de intergetijdengebieden van de Schelde inzake stikstofverwijdering in te schatten, en de factoren te quantificeren die de verwijderingscapaciteit bepalen. Bij de aanvang van de studie bleek echter dat een consistent beeld betreffende de waterkwaliteit van het hele estuarium inclusief het zoetwatergetijdengedeelte ontbrak. De karakterisatie van de waterkwaliteit was derhalve een tweede doel. Ten slotte was het de bedoeling om de kennis inzake waterkwaliteit aan te wenden om mogelijkheden tot herstel van het estuariene systeem af te leiden.

Bij de aanvang van de studie werden echter twee cruciale gebreken in de kennis vastgesteld. Het zoetwater deel van het Schelde-estuarium was quasi *terra incognita* wat ecologische kennis betrof, en de waterkwaliteitsdata van het hele estuarium waren versnipperd. De eerste lacune werd verholpen door een literatuurstudie betreffende de zoetwatergetijdengebieden van de wereld. Hieruit bleek dat zoetwatergetijdenzones van estuaria heel specifieke systemen zijn met eigen kenmerken die hen onderscheiden van rivieren. Het tweede hiaat werd verholpen door de bestaande data te integreren en een eigen estuarien monitoring op te zetten. De resultaten van 7 jaar eigen monitoring langsheen het Schelde-estuarium zijn voorgesteld, waarbij Nederlandse data van de Westerschelde en eigen data van het Belgische deel, de Zeeschelde, werden geïntegreerd. Dit resulteerde in een beschrijving van de waterkwaliteit van de monding tot de meeste opwaartse grens. Vanuit het oogpunt van het broeikaseffect werden de data verder geanalyseerd. Dit werd mogelijk gemaakt door een toevallige maar lineair consistente, jaargemiddelde stijging van de debieten over een periode van 5 jaar, van 28 $m^3 s^{-1}$ in 1996 tot 73 $m^3 s^{-1}$ in 2000. Deze debietsstijging werden gehanteerd als referentie voor toekomstige neerslagwijzigingen t.g.v. het broeikaseffect. Bij hoge debieten vertoonden nutriëntconcentraties (NH_4^+, NO_3^-, opgelost silicium en PO_4^{3-}) tot 50% afname van de concentratie terwijl de vrachten van deze nutriënten daarentegen toenamen tot zelfs 100%. De seizoensvariatie van de nutriënten werd getemperd door tegenstrijdige effecten van debiet op concentratie in de zomer versus tijdens de winter. Bij hoge debieten werd de opname van opgelost silicium door diatomeeën minder. De vracht opgelost silicium die de kustwateren bereikte steeg navenant.

Metingen van denitrificatie werden langsheen een longitudinale en verticale gradiënt van het Schelde-estuarium uitgevoerd a.h.v. de acetyleen inhibitie techniek, toegepast op stalen die in het laboratorium werden geïncubeerd. Uitstoot van N_2O werd tevens gemeten in het veld. Bijkomende experimenten werden uitgevoerd om limitering van nitraat vs. koolstof te bepalen, om zuurstofconsumptie te bepalen en om de rol van overspoelingsregime op de uitstoot van N_2O te bepalen. De variatie van denitrificatie (0.22 to 6.8 mmol N m^{-2} d^{-1}) en N_2O uitstoot (0.005 to 0.48 mmol N m^{-2} d^{-1} in laboratorium incubaties en 0 to 0.49 mmol N m^{-2} d^{-1} in het veld) was groot, zowel in ruimte als tijd. Hoewel nitraat limiterend bleek voor denitrificatie, nam dit proces toch af bij constante nitraataanvoer als het getij steeg. Zuurstofverbruik verbonden met de aanwezigheid van wormen was met .23 mol O^2 mol C^{-1} d^{-1} hoger dan voordien werd aangenomen. De hypothese wordt vooropgesteld dat de aanwezigheid van fauna in het sediment denitrificatie niet enkel stimuleert door vergemakkelijkt transport van nitraat maar ook door zuurstofverbruik in de water-sediment overgang. Aangezien een sterk reagerend gas is m.b.t. de broeikasgasproblematiek, werd een vergelijking gemaakt tussen de impact van de uitstoot van de onderlinge broeikasgassen. In vergelijking met de uitstoot van CO_2 en methaan is de uitstoot van N_2O uit het Schelde-estuarium te verwaarlozen. Ondanks de intense denitrificatiewaarden was de impact op de stikstofvracht in het estuarium gering.

De opmaak van massabalansen zijn een eenvoudig middel om de interactie tussen schorren en het water van een estuarium te bepalen. Een schor te Tielrode werd hiertoe geselecteerd. Tijdens de voortgang van dit doctoraat was echter vastgesteld dat de nutriëntverhoudingen in het estuarium verschoven waren. Het stikstofprobleem werd hierdoor iets minder precair. Daarom werden niet enkel van stikstof massabalansen opgemaakt, maar van een hele reeks parameters waaronder opgeloste zuurstof, nutriënten (N, P en Si), koolstof, chlorophyll, zwevende stof, chloride en zwavel. De rol van nasijpeling uit het schor werd eveneens bestudeerd. Een rangschikking van de parameters volgens de waargenomen effecten toonde dat zuurstofvoorziening aan het estuariene water de belangrijkste functie van het schor was. Alle parameters betreffende vaste deeltjes gaven import te zien in het schor. Export van silicium was belangrijker dan enig ander effect op nutriënten. Nochtans droegen export van opgelost silicium en import van totaal opgelost stikstof (TDIN) evenzeer bij tot de wijziging van de N:Si verhouding van het nasijpelingswater. Daarmee werkte het schor de trend tegen waarmee de nutriëntverhoudingen zich wijzigen in het estuarium.

Dynamische systemen zoals estuaria vereisen een aanpak die met deze dynamiek rekening houdt wanneer het gaat over de opmaak van doelen naar ecosysteemherstel. De gestelde

doelen moeten ook in voor het beleid makkelijk hanteerbare eenheden zijn uitgedrukt, zoals oppervlakteeenheden of valuta. Met het begrip draagkracht als centraal concept is een methode uitgewerkt om te bepalen hoeveel hectare slikgebied nodig is in een estuarium. Deze zgn. instandhoudingsdoelstelling ging uit van relaties tussen benthos, fytoplankton en waterkwaliteit. Verschillende scenario's werden uitgewerkt, elk met hun eigen historische areaalbeschikbaarheid en vuilvracht. Een bekkenmodel, met eraan gekoppeld een estuarien model, werd gebruikt om de waterkwaliteit van ongekende scenario's te reconstrueren. De vergelijking met de huidige toestand kon zo worden vergeleken. Als criterium om een scenario te bestempelen als 'goed' of 'onvoldoende' werd zuurstof als limiterende factor voor diversiteit gehanteerd. Voor het Belgische deel van het Schelde-estuarium, de Zeeschelde, kwamen het 'ongerepte' scenario (zonder menselijke aanwezigheid) en het '1950' scenario als geschikte referenties uit de bus. Vergelijking met de onvoldoende scenario's leverde een noodzaak op van 500 ha extra slikareaal bovenop het huidige areaal. De benadering heeft het voordeel dat ook de nodige reductie van de vuilvracht om een goede diversiteit te bekomen is gequantificeerd.

Vertrekkende van een systeem dat weinig gedocumenteerd was, werd aan het einde van deze studie een quantificering van enkele herstelnoden bereikt.

References

Alexandre A., Meunier J.-D., Colin F., Koud J.-M. (1997) Plant impact on the biogeochemical cycle of silicon and related weathering processes. Geochimica et Cosmochimica Acta 61: 677-682.

Allison L.E. (1965) Organic carbon. In: Black C.A. (Ed.) Methods of soil analysis, part 2. Madison, Wisconsin, America Society of Agronomy. Agronomy 9: 1367-1378.

Appeltans W., Hannouti A., Van Damme S., Soetaert K., Vanthomme R., Tackx M. (2004) Zooplankton in the Schelde estuary (Belgium/The Netherlands). The distribution of Eurytemora affinis: effect of oxygen? Journal of Plankton Research 25: 1441-1445.

Arnell P.W. (1999) The effect of climate change on hydrological regimes in Europe: a continental perspective. Global Environmental Change-Human and Policy Dimensions 9: 5-23.

Asmus R.M., Sprung M., Asmus H. (2000) Nutrient fluxes in intertidal communities of a South European lagoon (Ria Formosa) – similarities and differences with a northern Wadden Sea bay (Sylt-Rømø Bay). Hydrobiologia 436: 217-235.

Bacon R. (1997) Nitrate preserved sausage meat causes an unusual food poisoning incident. Communicable Disease Report 7: 45-47.

Baeyens W. (1998) Evolution of trace metal concentrations in the Scheldt estuary (1978-1995). A comparison with estuarine and ocean levels. Hydrobiologia 366, 157-167.

Bakker C., Heerebout G.R. (1971) De verontreiniging van de Westerschelde. Hydrobiological Bulletin 5: 53-64.

Baldwin A.H., Barendregt A., Whigham D. (2009) Tidal freshwater wetlands – an introduction to the ecosystem. In: Barendregt A., Whigham D., Baldwin A.H. (Eds) Tidal freshwater wetlands. Blackhuys Publishers, Leiden, the Netherlands, pp. 1-10.

Balls P.W., Brockie N., Dobson J., Johnston W. (1996) Dissolved oxygen and nitrification in the upper Forth estuary during summer (1982-92): Patterns and trends. Estuarine, Coastal and Shelf Science 42: 117-134.

Barendregt A., Whigham D., Meire P., Baldwin A., Van Damme S. (2006) Wetlands in the tidal freshwater zone. In: Bobbink R., Beltman B., Verhoeven J.T.A., Whigham D.F. (Eds) Wetlands: Functioning, biodiversity conservation, and restoration. Ecological Studies - Volume 191, Springer Verlag, Berlin, pp. 117-148.

Baretta-Bekker H.J., Duursma E.K., Kuipers B.R. (1998) Encyclopedia of marine sciences. Springer Verlag, Berlin, 367 pp.

Bartoli F. (1983) The biogeochemical cycle of silicon in two temperate forest ecosystems. Ecological Bulletin 35: 469-476.

Billen G. (1975) Nitrification in the Scheldt estuary (Belgium and The Netherlands). Estuarine, Coastal and Marine Science 3: 79-89.

Billen G. (1993) Coastal eutrophication in a global perspective. In: Symoens J.-J., Devos P., Rammeloo J., Verstraeten Ch. (Eds) Biological indicators of global change. Symposium proceedings, Royal Academy of Overseas Sciences, Brussels, pp. 17-34.

Billen G., Garnier J. (1997) The Phison River plume: coastal eutrophication in response to changes in land use and water management in the watershed. Aquatic Microbial Ecology 13: 3-17.

Billen G., Garnier J. (1999) Nitrogen transfer through the Seine drainage network: a budget based on the application of the RIVERSTRAHLER Model. Hydrobiologia 410: 139-150.

Billen G., Garnier J., Ficht A., Cun C. (2001) Modeling the response of water quality in the Seine river estuary to human activity in its watershed over the last 50 years. Estuaries 24: 977-993.

Billen G., Garnier J., Rousseau V. (2005) Nutrient fluxes and water quality in the drainage network of the Scheldt basin over the last 50 years. Hydrobiologia 540: 47-67.

Billen G., Lancelot C., Meybeck M. (1991) N, P and Si retention along the aquatic continuum from land to ocean. In Mantoura R.F.C., Martin J.M., Wollast R. (Eds) Ocean margin processes in global change. John Wiley & Sons, Chichester, pp. 19-44.

Billen G., Somville M. (1982) An ecophysiological model of nitrification in the Scheldt estuary. Mathematical Modelling 3: 523-533.

Billen G., Somville M., De Becker E., Servais P. (1985) A nitrogen budget of the Scheldt hydrographical basin. Netherlands Journal of Sea Research 19: 223-230.

Boderie P.M.A., Zwolsman J.J.G., Van Eck G.T.M., Van Der Weijden C.H. (1993) Nutrient biogeochemistry in the water column (N, P, Si) and pore-water (N) of sandy sediment of the Scheldt estuary (SW-Netherlands). Netherlands Journal of Aquatic Ecology 27: 309-318.

Boeckx P., Van Cleemput O. (2001) Estimates of N_2O and CH_4 fluxes from agricultural lands in various regions in Europe. Nutrient Cycling in Agroecosystems 60: 35-47.

Boesch D.F. (2002) Challenges and opportunities for science in reducing nutrient over-enrichment of coastal ecosystems. Estuaries 25: 886-900.

Boesch D.F., Brinsfield R.B., Magnien R.E. (2001) Chesapeake Bay eutrophication: Scientific understanding, ecosystem restoration, and challenges for agriculture. Journal of Environmental Quality 30: 303-320.

Borja A., Franco J., Perez V. (2000) A marine Biotic Index to establish the ecological quality of soft-bottom benthos within European estuarine and coastal environments. Marine Pollution Bulletin, 40: 1100-1114.

Borum J., Sand-Jensen K. (1996) Is total primary production in shallow coastal marine waters stimulated by nitrogen loading? Oikos 76: 406-410.

Bowden W.B. (1984) A nitrogen-15 isotope dilution study of ammonium production and consumption in a marsh sediment. Limnology and Oceanography 29: 1004-1015.

Bowden W.B. (1986) Nitrification, nitrate reduction, and nitrogen immobilization in a tidal freshwater marsh sediment. Ecology 67: 88-99.

Bowden W.B. (1987) The biogeochemistry of nitrogen in freshwater wetlands. Biogeochemistry 4: 313-348.

Bowden W.B., Vörösmarty C.J., Morris J.T., Peterson B.J., Hobbie J.E., Steudler P.A., Moore B. (1991) Transport and processing of nitrogen in a tidal freshwater wetland. Water Resources Research 27: 389-408.

Brasse S., Nellen M., Seifert R., Michaelis W. (2002) The carbon dioxide system in the Elbe estuary. Biogeochemistry 59: 25-40.

Bremner J.M. (1965a) Inorganic forms of nitrogen. In: Black C.A. (Ed.) Methods of soil analysis, part 2. Madison, Wisconsin, America Society of Agronomy. Agronomy 9: 1179-1237.

Bremner J.M. (1965b) Total nitrogen. In: Black C.A. (Ed.) Methods of soil analysis, part 2. Madison, Wisconsin, America Society of Agronomy. Agronomy 9: 1149-1178.

Brion N., Billen G., Guezennec L., Ficht A. (2000) Distribution of nitrifying activity in the Seine River (France) from Paris to the estuary. Estuaries 23: 669-682.

Brockmann U., Billen G., Gieskes W.W.C. (1988) North Sea nutrients and eutrophication . In: Salomons W., Bayne B.L., Duursma E.K., Förstner U. (Eds) Pollution of the North Sea. An assessment. Springer, Berlin, pp. 348-389.

Buchanan C., Lacouture R.V., Marshall H.G., Olson M., Johnson J.M. (2005) Phytoplankton reference communities for Chesapeake Bay and its tidal tributaries. Estuaries 28: 138-159.

Burchard H., Baumert H. (1998) The formation of estuarine turbidity maxima due to density effects in the salt wedge. A hydrodynamic process study. Journal of Physical Oceanography 28: 309-321.

Cai W., Wiebe W.J., Wang Y., Sheldon J.E. (2000) Intertidal marsh as a source of dissolved inorganic carbon and a sink of nitrate in the Satilla river-estuarine complex in the southeastern U.S. Limnology and Oceanography 45: 1743-1752.

Capers R.S. (2003) Six years of submerged plant community dynamics in a freshwater tidal wetland. Freshwater Biology 48: 1640-1651.

Caraco N.F., Cole J.J., Likens G.E., Lovett G.M., Weathers K.C. (2003) Variation in NO_3 export from flowing waters of vastly different sizes: Does one model fit all? Ecosystems 6: 344-352.

Chambers R.M., Odum W.E. (1990) Porewater oxidation, dissolved phosphate and the iron curtain: Iron-phosphorous relations in tidal freshwater marshes. Biogeochemistry 10: 37-52.

Chatarpaul L., Robinson J.B., Kaushik N.K. (1980) Effects of tubificid worms on denitrification and nitrification in stream sediment. Canadian Journal of Fisheries and Aquatic Science 37: 656-663.

Chen M., Wartel S., Van Eck G.T.M., Van Maldegem D.C. (2005) Suspended matter in the Scheldt estuary. Hydrobiologia 540: 79-104.

Childers D.L., Cofer-Shabica S., Nakashima L. (1993) Spatial and temporal variability in marsh-water column interactions in a southeastern USA salt marsh estuary. Marine Ecology Progress Series 95: 25-38.

Childers D.L., Day Jr. J.W. (1988) A flow-through flume technique for quantifying nutrient and materials fluxes in microtidal estuaries. Estuarine, Coastal and Shelf Science 27: 483-494.

Christensen P., Pauly D. (1998) Changes in models of aquatic ecosystems approaching carrying capacity. Ecological Applications 8: S104-S109.

Cloern J.E. (1987) Turbidity as a control on phytoplankton biomass and productivity in estuaries. Continental Shelf Research 5: 1367-1381.

Cloern J.E. (1999) The relative importance of light and nutrient limitation of phytoplankton growth: A simple index of coastal ecosystem sensitivity to nutrient enrichment. Aquatic Ecology 33: 3-16.

Cloern J.E. (2001) Our evolving conceptual model of the coastal eutrophication problem. Marine Ecology Progress Series 210: 223-253.

Coen I. (1988) Ontstaan en ontwikkeling van de Westerschelde (with summary). Water 43: 156-162.

Cohen J.E. (1997) Population, economics, environment and culture: An introduction to human carrying capacity. Journal of Applied Ecology 34: 1325-1333.

Cole J.J., Caraco N.F., Peierls B.L. (1992) Can phytoplankton maintain a positive carbon balance in a turbid, fresh-water, tidal estuary? Limnology and Oceanography 37: 1608-1617.

Colijn F., Admiraal W., Baretta W.J., Ruardij P. (1987) Primary production in a turbid estuary, the Ems-Dollard - Field and model studies. Continental Shelf Research 7: 1405-1409.

Conley D.J. (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochemical Cycles 16: 1121.

Cooper S.R., Brush G.S. (1993) A 2500-year history of anoxia and eutrophication in Chesapeake Bay. Estuaries 16: 617-626.

Corell D.L. (1998) The role of phosforous in the eutrofication in receiving waters: A review. Journal of Environmental Quality 27: 261-266.

Correll D.L., Jordan T.E., Weller D.E. (1992) Nutrient flux in a landscape: effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. Estuaries 15: 431-442.

Correll D.L., Jordan T.E., Weller D.E. (2000) Dissolved silicate dynamics of the Rhode river watershed and estuary. Estuaries 23: 188-198.

Costanza R., d'Arge R., de Groot R., Farber S., Gasso M., Hannon B., Limburg K., Naeem S., O'Neill R.V., Paruelo J., Raskin R.G., Sutton P., van den Belt M. (1997) The value of the world's ecosystem services and natural capital. Nature 387: 253-260.

Costanza R., Kemp W.M., Boynton W.R. (1993) Predictability, scale, and biodiversity in coastal and estuarine ecosystems: implications for management. Ambio 22: 88-96.

Cox T., Maris T., Soetaert K., Conley D., Van Damme S., Meire P., Middelburg J.J., Vos M., Struyf E. (2009) A macrotidal freshwater ecosystem recovering from hypereutrophication: the schelde case study. Biogeosciences 6: 2935-2948.

Cugier P., Billen G., Guillaud J.F., Garnier J., Ménesguen A. (2005) Modelling the eutrophication of the Seine Bight (France) under historical, present and future riverine nutrient loading. Journal of Hydrology 304: 381-396.

Curran J.C., Robertson M. (1991) Water quality implications of an observed trend of rainfall and runoff. Journal of the Institution of Water and Environmental Management 5: 419-424.

Dame R., Chrzanowski T., Bildstein K., Kjerfve B., Mckellar H., Nelson D., Spurrier J., Stancyk S., Stevenson H., Vernberg J., Zingmark R. (1986) The outwelling hypothesis and North Inlet, South Carolina. Marine Ecology Progress Series 33: 217-229.

Dankers N., Binsbergen M., Zegers K., Laane R., Rutgers van der Loeff M. (1984) Transport of water, particulate and dissolved organic and inorganic matter between a salt marsh and the Ems-Dollard estuary, The Netherlands. Estuarine, Coastal and Shelf Science 19: 143-165.

Dean T.L., Richardson J. (1999) Responses of seven species of native freshwater fish and a shrimp to low levels of dissolved oxygen. New Zealand Journal of Marine and Freshwater Research 33: 99-106.

de Bie M.J.M., Starink M., Boschker H.T.S., Peene J.J., Laanbroek H.J. (2002) Nitrification in the Schelde estuary: methodological aspects and factors influencing its activity. FEMS Microbial Ecology 42: 99-107.

de Groot R.S., Wilson M.A., Boumans R.M.J. (2002) A typology for the classification, description and valuation of ecosystem functions, goods and services. Ecological Economics 41: 393-408.

de Jonge V.N., D.J. de Jong (2002) Ecological restoration in coastal areas in the Netherlands: concepts, dilemmas and some examples. Hydrobiologia 478: 7-28.

Del Monte-Luna P., Brook B.W., Zetina-Rejon M.J., Cruz-Escalona V.H. (2004) The carrying capacity of ecosystems. Global Ecology and Biogeography 13: 485-495.

De Pauw N. (1971) Milieu en plankton in de Westerschelde. Hydrobiological Bulletin 5: 3-16.

De Pauw N. (1975) Contribution to the knowledge of environment and plankton in the Westerschelde estuary. Ph.D. Thesis, Ghent University, Faculty of Sciences, Gent, Belgium. (in Dutch).

De Pillecyn F. (1950) De veerman en de jonkvrouw. De Clauwaert, Leuven, 194 pp.

Desmit X., Vanderborght J.P., Regnier P., Wollast R. (2005) Control of phytoplankton production by physical forcing in a strongly tidal, well-mixed estuary. Biogeosciences 2: 205-218.

Dettmann E.H. (2001) Effect of water residence time on annual export and denitrification of nitrogen in estuaries: A model analysis. Estuaries 24: 481-490.

de Wilde H.P.J., de Bie M.J.M. (2000) Nitrous oxide in the Schelde estuary: production by nitrification and emission to the atmosphere. Marine Chemistry 69: 203-216.

Dippner J.W. (1998) Competition between different groups of phytoplankton for nutrients in the southern North Sea. Journal of Marine Systems 4: 181-198.

Doering P.H. (1996) Temporal variability of water quality in the St. Lucie estuary, South Florida. Water Resources Bulletin 32: 1293-1306.

Donner S.D., Coe M.T., Lenters J.D., Twine T.E., Foley J.A. (2002) Modeling the impact of hydrological changes on nitrate transport in the Mississippi River Basin from 1955 to 1994. Global Biogeochemical Cycles 16: 1-19.

Ducrotoy J.P., Elliott M., De Jonge V.N. (2000) The North Sea. Marine Pollution Bulletin 41: 5-23.

Dyer K.R. (1989) Sediment processes in estuaries: Future research requirements. Journal of Geophysical Research 94: 14327-14339.

Eisma D. (1986) Flocculation and de-flocculation of suspended matter in estuaries. Netherlands Journal of Sea Research 20: 183-199.

Elliott M., Burdon D., Hemingway K.L., Apitz S.E. (2007) Estuarine, coastal and marine ecosystem restoration: Confusing management and science - A revision of concepts. Estuarine, Coastal and Shelf Science 74: 349-366.

Elliott M., Cutts N. (2004) Marine Habitats: Loss and Gain, Mitigation and Compensation. Marine Pollution Bulletin 49: 671-674

Elliott M., McLusky D.S. (2002) The need for definitions in understanding estuaries. Estuarine, Coastal and Shelf Science 55: 815-827.

Escaravage V., Prins T.C. (2002) Silicate availability, vertical mixing and grazing control of phytoplankton blooms in mesocosms. Hydrobiologia 484: 33-48.

Fisher B., Turner R.K., Morling P. (2009) Defining and classifying ecosystem services for decision making. Ecological Economics 68: 643-653.

Flynn K.J. (2005) Castles built on sand: Dysfunctionality in plankton models and the inadequacy of dialogue between biologists and modellers. Journal of Plankton Research 27: 1205-1210.

Frankignoulle M., Abril G., Borges A., Bourge I., Canon C., Delille B., Libert E., Theate J.-M. (1998) Carbon dioxide emission from European estuaries. Science 282: 434-436.

Frankignoulle M., Bourge I., Wollast R. (1996) Atmospheric CO_2 fluxes in a highly polluted estuary (the Scheldt). Limnology and Oceanography 41: 365-369.

Froelich P.N. (1988) Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnology and Oceanography 33: 649-668.

Garcia-Ruiz R., Pattinson S.N., Whitton B.A. (1998) Denitrification in sediments of the freshwater tidal Yorkshire Ouse. The Science of the Total Environment 210/211: 321-327.

Garnier J., Billen G., Coste M. (1995) Seasonal succession of diatoms and Chlorophyceae in the drainage network of the Seine River: Observations and modelling. Limnology and Oceanography 40: 750-765.

Garnier J., Cebron A., Tallee G., Billen G., Sebilo M., Martinez A. (2006) Nitrogen behaviour and nitrous oxide emission in the tidal Seine River estuary (France) as influenced by human activities in the upstream watershed. Biogeochemistry 77: 305-326.

Garnier J., Servais P., Billen G., Akopian M., Brion N. (2001) Lower Seine river and estuary (France) carbon and oxygen budgets during low flow. Estuaries 24: 964-976.

Gellens D., Roulin E. (1998) Streamflow response of Belgian catchments to IPCC climate change scenarios. Journal of Hydrology 210: 242-258.

Gibbs R.J. (1970) Mechanisms controlling world water chemistry. Science 170: 1088-1090.

Glantz M.H. (1992) Climate variability, climate change, and fisheries, Cambridge University Press, New York, 450 p.

Gocke K., Lenz J. (2004) A new 'turbulence incubator' for measuring primary production in non-stratified waters. Journal of Plankton Research 26: 357-369.

Godin G. (1999) The propagation of tides up rivers with special considerations on the Upper Saint Lawrence river. Estuarine, Coastal and Shelf Science 48: 307-324.

Goosen N.K., Kromkamp J.J., Peene J., van Rijswijk P., van Breugel P. (1999) Bacterial and phytoplankton production in the maximum turbidity zone of three European estuaries: the Elbe, Westerschelde and Gironde. Journal of Marine Systems 22: 151-171.

Goosen N.K., Van Rijswijk P., Brockmann U. (1995) Comparison of heterotrophic bacterial production rates in early spring in the turbid estuaries of the Scheldt and the Elbe. Hydrobiologia 311: 31-42.

Grabemann I., Krause G. (2001) On different time scales of suspended matter dynamics in the Weser estuary. Estuaries 24: 688-698.

Grabemann I., Uncles R.J., Krause G., Stephens J.A. (1997) Behaviour of turbidity maxima in the Tamar (U.K.) and Weser (F.R.G.) estuaries. Estuarine, Coastal and Shelf Science 45: 235-246.

Gray J.S. (1992) Biological and ecological effects of marine pollution and their detection. Marine Pollution Bulletin 25: 48-50.

Gray J. S. (1997) Marine biodiversity: patterns, threats and conservation needs. Biodiversity and Conservation 6: 153-175.

Gribsholt B., Boschker H.T.S., Struyf E., Andersson M.G.I., Tramper A., De Brabandere L., Van Damme S., Brion N., Meire P., Dehairs F., Middelburg J.J. and Heip C. (2005) Nitrogen processing in a tidal freshwater marsh: a whole ecosystem ^{15}N labeling study. Limnology and Oceanography 50: 1945-1959.

Gribsholt B., Struyf E., Tramper A., Andersson M.G.I., Brion N., De Brabandere L., Van Damme S., Meire P., Middelburg J.J., Dehairs F., Boschker H.T.S. (2006) Ammonium transformation in a nitrogen-rich tidal freshwater marsh. Biogeochemistry 80: 289-298.

Grobbelaar J.U. (1990) Modelling phytoplankton productivity in turbid waters with small euphotic to mixing depth ratios. Journal of Plankton Research 12: 923-931.

Gruber N., Galloway J.N. (2008) An Earth-system perspective of the global nitrogen cycle. Nature 451: 293-296.

Guézennec L., Lafite R., Dupont J.P., Meyer R., Boust D. (1999) Hydrodynamics of suspended particulate matter in the tidal freshwater zone of a macrotidal estuary (the Seine estuary, France). Estuaries 22: 717-727.

Hamels I., Sabbe K., Muylaert K., Barranguet C., Lucas C., Herman P., Vyverman W. (1998) Organisation of microbenthic communities in intertidal estuarine flats, a case study from the Molenplaat (Westerschelde estuary, The Netherlands). European Journal of Protistology 34: 308-320.

Hargrave A.P., Shaykewich C.F. (1997) Rainfall induced nitrogen and phosphorus losses from Manitoba soils. Canadian Journal of Science 77: 59-65.

Heip C. (1988) Biota and abiotic environments in the Westerschelde estuary. Hydrobiological Bulletin 22: 31-34.

Heip C., Goosen N.K., Herman P.M.J., Kromkamp J., Middelburg J.J., Soetaert K. (1995) Production and consumption of biological particles in temperate tidal estuaries. Oceanography and Marine Biology: An Annual Review 33: 1-149.

Hellings L., Dehairs F., Tackx M., Keppens E., Baeyens W. (1999) Origin and fate of organic carbon in the freshwater part of the Scheldt estuary as traced by stable carbon isotope composition. Biogeochemistry 47: 167-186.

Hellings L., Dehairs F., Van Damme S., Baeyens W. (2001) Dissolved inorganic carbon in a highly polluted estuary (the Scheldt). Limnology and Oceanography 46: 1406-1414.

Herman P.M.J., Middelburg J.J., Van de Koppel J., Heip C.H.R. (1999) Ecology of estuarine macrobenthos. Advanced Ecological Research 29: 195-240.

Herman P.J.M., Middelburg J.J., Widows J., Lucas C.H., Heip C.H.R. (2000) Stable isotopes as trophic tracers: combining field sampling and manipulative labelling of food resources for macrobenthos. Marine Ecology Progress Series 204: 79-92.

Hermes-Lima M., Zenteno-Savin T. (2002) Animal response to drastic changes in oxygen availability and physiological oxidative stress. Comparative Biochemistry and Physiology 133: 537-556.

Hofmann A.F., Soetaert K., Middelburg J. (2008) Present nitrogen and carbon dynamics in the Scheldt estuary using a novel 1-D model. Biogeosciences 5: 981-1006.

Holligan P.M., Reiners W.A. (1992) Predicting the responses of the coastal zone to global change. Advances in Ecological Research 22: 211-255.

Horrevoets A.C., Savenije H.H.G., Schuurman J.N., Graas S. (2004) The influence of river discharge on tidal damping in alluvial estuaries. Journal of Hydrology 294: 213-228.

Howarth R.W. (1988) Nutrient limitation of net primary production in marine ecosystems. Annual Review of Ecology and Systematics 19: 89-110.

Howarth R.W., Billen G., Swaney D. (1996) Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry 35: 181-226.

Howarth RW, Schneider R., Swaney D. (1996) Metabolism and organic carbon fluxes in the tidal freshwater Hudson River. Estuaries 19: 846-665.

Howarth R.W., Swaney D.P., Butler T.J., Marino R. (2000) Climatic control on eutrophication of the Hudson River estuary. Ecosystems 3: 210-215.

Hummel H., Moerland G., Bakker C. (1988) The concomitant existence of a typical coastal and a detritus food chain in the Westerschelde estuary. Hydrobiological Bulletin 22: 35-41.

Hutchinson G.E. (1957) A treatise on limnology, volume I. Geography, physics and chemistry. John Wiley & Sons, New York, 1015 pp.

Jackson R.H., Williams P.J., Le B., Joint I.R. (1987) Freshwater phytoplankton in the low salinity region of the River Tamar estuary. Estuarine, Coastal and Shelf Science 25: 299-311.

Jacobs S., Struyf E., Maris T., Meire P. (2008) Spatiotemporal aspects of silica buffering in restored tidal marshes. Estuarine, Coastal and Shelf Science 80: 42-52.

Jensen M.M., Thamdrup B., Dalsgaard T. (2007) Effects of specific inhibitors on annamox and denitrification in marine sediments. Applied Environmental Microbiology 73: 3151-3158.

Jordan T.E., Corell D.L. (1991) Continuous automated sampling of tidal exchanges of nutrients by brackish marshes. Estuarine, Coastal and Shelf Science 32: 527-545.

Jordan T.E., Correll D.L., Miklas J., Weller D.E. (1991) Long-term trends in estuarine nutrients and chlorophyll, and short-term effects of variations in watershed discharge. Marine-Ecology Progress Series 75 121-132.

Jordan T.E., Corell D.L., Miklas J. Weller D.E. (1991) Nutrients and chlorophyll at the interface of a watershed and an estuary. Limnology and Oceanography 36: 251-267.

Justic D., Rabalais N.N., Turner R.E. (1997) Impacts of climate change on net productivity of coastal waters: implications for carbon budgets and hypoxia. Climate Research 8: 225-237.

Khan H. Brush G.S. (1994) Nutrient and metal accumulation in a freshwater tidal marsh. Estuaries 17: 345-360.
Kies L. (1997) Distribution, biomass and production of planktonic and benthic algae in the Elbe estuary. Limnologica 27: 55-64.
Kondratyev K.Y., Pozdnyakov D.V. (1996) Land-ocean interactions in the coastal zone: the LOICZ project. Il Nuovo Cimento 19: 339-354.
Krieg H.-J. (2005) Die entwicklung eines modifizierten Potamon-Typie-Indexes zur Bewertung des ökologischen Zustands der Tideelbe von Geesthacht bis zur Seegrenze. ARGE ELBE – FHH/BSU – WG Elbe, Hamburg, 42 pp.
Krom M.D., Berner R.A. (1980) The diagenesis of phosphorus in a nearshore marine sediment. Geochimica et Cosmochimica Acta 45: 207-216.
Kromkamp J.C., Peene J. (2005) Changes in phytoplankton biomass and primary production between 1991 and 2001 in the Westerschelde estuary (Belgium/The Netherlands). Hydrobiologia 540: 117-126.
Kromkamp J., Peene J., van Rijswijk P., Sandee A., Goosen N. (1995) Nutrients, light and primary production by phytoplankton and microphytobenthos in the eutrophic, turbid Westerschelde estuary (The Netherlands). Hydrobiologia 311: 9-19.
Lampman G.G., Caraco N.F., Cole J.J. (1999) Spatial and temporal patterns of nutrient concentration and export in the tidal Hudson River. Estuaries 22: 285-296.
Lancelot C. (1995) The mucilage phenomenon in the continental coastal waters of the North-Sea. Science of the Total Environment 165: 83-102.
Lancelot C., Billen G., Sournia A., Weisse T., Colijn F., Veldhuis M., Davies A., Wassman P. (1987) Phaeocystis blooms and nutrient enrichment in the continental coastal zone of the North Sea. Ambio 16: 38-47.
Laverman A.M., Meile C., Van Capellen P., Wieringa E.B.A. (2007) Vertical distribution of denitrification in an estuarine sediment: integrating sediment flowthrough reactor experiments and microprofiling via reactive transport modeling. Applied and Environmental Microbiology 73: 40-47.
Laverman A.M., Van Capellen P., Van Rotterdam-Los D., Pallud C., Abell J. (2006) Potentail rates and pathways of microbial nitrate reduction in coastal sediments. Microbial Ecology 58: 179-192.
Lesourd S., Lesueur P., Brun-Cottan J-C., Auffret J-P., Poupinet N., Laignel B. (2001) Morphosedimentary evolution of the macrotidal Seine estuary subjected to human impact. Estuaries 24: 940-949.
Lindsay P., Balls P.W., West J.R. (1996) Influence of tidal range and river discharge on suspended particulate matter fluxes in the Forth estuary (Scotland). Estuarine, Coastal and Shelf Science 42: 63-82.
Lionard M., Muylaert K., Van Gansbeke D., Vyverman W. (2005) Influence of changes in salinity and light intensity on growth of phytoplankton communities from the Schelde river and estuary (Belgium/The Netherlands). Hydrobiologia 540: 105-115.
Lowrance R., Leonard R., Sheridan J. (1985) Managing riparian ecosystems to control non-point pollution. Journal of Soil and Water Concentration 40: 87-97.
Lucas Y., Luizao F.J., Chauvel A., Rouiller J., Nahon D. (1993) The relation between biological activity of the rain forest and mineral composition of soils. Science 260: 521-523.
MacLeod M., Cooper J.A.G. (2005) Carrying capacity in coastal areas. In: Schwartz M. (Ed.) Encyclopedia of coastal science. Springer, 226 pp.
Maes J., Stevens M., Breine J. (2008) Poor water quality constrains the distribution and movements of twaid shad *Alosa fallax* (Lacépède, 1803) in the watershed of river Scheldt. Hydrobiologia 602: 129-143.
Maes J., Taillieu A., Van Damme P.A., Cottenie K., Ollevier F. (1998) Seasonal patterns in the fish and crustacean community of a turbid temperate estuary (Zeeschelde estuary, Belgium). Estuarine, Coastal and Shelf Science 47: 143-151.
Maes J., Van Damme S., Meire P., Ollevier F. (2004) Statistical modeling of seasonal and environmental influences on the population dynamics of an estuarine fish community. Marine Biology 145: 1033-1042.
Mann K.H. (1988) Production and use of detritus in various freshwater, estuarine and coastal marine ecosystems. Limnology and Oceanography 33: 910-930.
Meire P., Vincx M. (Eds) (1993) Marine and estuarine gradients. Netherlands Journal of Aquatic Ecology 27 Nr 2-4.
Meire P., Ysebaert T., Van Damme S., Van den Bergh E., Maris T., Struyf E. (2005) The Scheldt estuary from past to future: a description of a changing ecosystem. Hydrobiologia 540: 1-11.
Meyer R.L., Risgaard-Petersen N., Allen D.E. (2005) Correlation between anammox activity and microscale distribution of nitrite in a subtropical mangrove sediment. Applied and Environmental Microbiology 71: 6142–6149.
Middelburg J.J., Klaver G., Nieuwenhuize J., Markusse R.M., Vlug T., Van der Nat F.W.J.A. (1995b) Nitrous oxide emissions from estuarine intertidal sediments. Hydrobiologia 311: 43-55.
Middelburg J.J., Klaver G., Nieuwenhuize J., Vlug T. (1995a) Carbon and nitrogen cycling in intertidal sediments near Doel, Scheldt estuary. Hydrobiologia 311: 57-69.

Middelburg J.J., Klaver G., Nieuwenhuize J., Wielemaker A., de Haas W., Vlug T., Van der Nat J.F.W.A. (1996) Organic matter mineralisation in intertidal sediments along an estuarine gradient. Marine Ecology Progress Series 132: 157-168.

Middelburg J.J., Nieuwenhuize J., Iversen N., Høgh N., de Wilde H., Helder W., Seifert R., Christof O. (2002) Methane distribution in European tidal estuaries. Biogeochemistry 59: 95-119.

Mitchell J.F.B. (1989) The greenhouse effect and climate change. Review of Geophysics 27: 115-139.

Monbet Y. (1992) Control of phytoplankton biomass in estuaries: A comparative analysis of microtidal and macrotidal estuaries. Estuaries 15: 563-571.

Moon C. Dunstan W.M. (1990) Hydrodynamic trapping and the formation of the chlorophyll *a* peak in the turbid, very low salinity waters of estuaries. Journal of Plankton Research 12: 323-336.

Moraghan J.T., Buresh R. (1977) Correction for dissolved nitrous oxide in nitrogen studies. Soil Science Society of America Journal 41: 1201-1202.

Morris J.T. (1995) The mass-balance of salt and water in intertidal sediments- results from North-Inlet, South Carolina. Estuaries 18: 556-567.

Muller-Solger A.B., Jassby A.D., Muller-Navarra D.C. (2002) Nutritional quality of food resources for zooplankton (Daphnia) in a tidal freshwater system (Sacramento-San Joaquin River Delta). Limnology and Oceanography 47: 1468-1476.

Muylaert K., Sabbe K. (1999) Spring phytoplankton assemblages in and around the maximum turbidity zone of the estuaries of the Elbe (Germany), the Schelde (Belgium/The Netherlands) and the Gironde (France). Journal of Marine Systems 22: 133-149.

Muylaert K., Sabbe K., Vyverman W. (2000a) Spatial and temporal dynamics of phytoplankton communities in a freshwater tidal estuary (Schelde, Belgium). Estuarine Coastal and Shelf Science 50: 673-687.

Muylaert K., Tackx M., Vyverman W. (2005) Phytoplankton growth rates in the freshwater tidal reaches of the Schelde estuary (Belgium) estimated using a simple light-limited primary production model. Hydrobiologia 540: 127-140.

Muylaert K., Van Kerkvoorde A., Vyverman W., Sabbe K. (1997) Structural characteristics of phytoplankton assemblages in tidal and non-tidal freshwater systems: a case-study from the Schelde basin. Freshwater Biology 38: 263-276.

Muylaert K., Van Mieghem R., Sabbe K., Tackx M., Vyverman W. (2000b) Dynamics and trophic roles of heterotrophic protists in the plankton of a freshwater tidal estuary. Hydrobiologia 432: 25-36.

Muylaert K., Van Nieuwerburgh L., Sabbe K., Vyverman W. (2002) Microphytobenthos communities in the freshwater tidal to brackish reaches of the schelde estuary (Belgium) Belgian Journal of Botany 135: 15-26.

Muylaert K., Van Wichelen J., Sabbe K., Vyverman W. (2001) Effects of freshets on phytoplankton dynamics in a freshwater tidal estuary (Schelde, Belgium). Archiv fur Hydrobiologie 150: 269-288.

Muylaert K., Vyverman W. (2006) Impact of a flood event on the planktonic food web of the Schelde estuary (Belgium) in spring 1998. Hydrobiologia 559: 385-394.

Neal C., Jarvie H.P., Whitton B.A., Gemmell J. (2000) The water quality of the River Wear, North-East England. Science of the Total Environment 251: 153-172.

Nijssen B., O'Donnell G.M., Hamlet A.F., Lettenmaier D.P. (2001) Hydrologic sensitivity of global rivers to climate change. Climatic Change 50: 143-175.

Nixon S.W. (1990) Marine eutrophication: A growing international problem. Ambio 19: 101.

Nixon S.W., Ammerman J.W., Atkinson L.P. (1996) The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35: 141-180.

Odum W.D. (1988) Comparative ecology of tidal freshwater and salt marshes. Annual Review of Ecology and Systematics 19: 147-176.

Officer C.B., Ryther J.H. (1980) The possible importance of silicon in marine eutrophication. Marine Ecology Progress Series 3: 83-91.

O'Shea M.L., Brosnan T.M. (2000) Trends in indicators of eutrophication in Western Long Island Sound and the Hudson-Raritan Estuary. Estuaries 23: 877-901.

Ouboter M.R.L., Van Eck B.T.M., Van Gils J.A.G., Sweerts J.P., Villars M.T. (1998) Water quality modelling of the western Scheldt estuary. Hydrobiologia 366: 129-142.

Paine R.T. (1966) Food web complexity and species diversity. American Naturalist 100: 850-860.

Peeters J.C.H., Peperzak L. (1990) Nutrient limitation in the North Sea: a bioassay approach. Netherlands Journal of Sea Research 26: 61-73.

Pelegri S.P., Blackburn T.H. (1995) Effects of *Tubifex tubifex* (Oligochaeta: Tubificidae) on N-mineralisation in freshwater sediments, measured with ^{15}N isotopes. Aquatic Microbial Ecology 9: 289-294.

Platt T., Lewis M., Geider R. (1984) Thermodynamics of the pelagic ecosystem: Elementary closure conditions for biological production in the open ocean. In: Fasham M.J.R. (Ed.) Flows of energy and materials in marine ecosystems. Plenum Press, New York, USA, pp. 48-84.

Postma H. (1967) Sediment transport and sedimentation in the estuarine environment. In: Lauff G.H. (Ed.) Estuaries. Publ. no. 83. American Association of Advanced Science, Washington, pp. 158-179.

Postma H., Kalle K. (1955) Die Entstehung von Trübungszonen im Unterlauf der Flüsse, speziell im Hinblick auf die Verhältnisse in der Unterelbe. Deutsche Hydrographische Zeitschrift 8: 138-144.

Postma H., Zijlsta J.J. (1988) Continental shelves. Ecosystems of the world, 27. Elsevier, Amsterdam, 421 pp.

Rabalais N.N., Turner R.E., Justic' D., Dortsch Q., Wiseman Jr. W.J., Sen Gupta B. (1996) Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. Estuaries 19: 386-407.

Reddy K.R., Patrick Jr. W.H., Lindau C.W. (1989) Nitrification-denitrification at the plant root sediment interface in wetlands. Limnology and Oceanography 34: 1004-1013.

Regnier P., Wollast R., Steefel C.I. (1997) Long-term fluxes of reactive species in macrotidal estuaries: estimates from a fully transient, multicomponent reaction-transport model. Marine Chemistry 58: 127-145.

Rehbehn R., Schuchardt B., Schirmer M., Kirst G.O. (1993) The distribution of *Actinocyclus normanii* (Bacillariophyceae) in estuaries: Field observations and laboratory investigations. Netherlands Journal of Aquatic Ecology 27: 205-214.

Rich J.J., Dale O.R., Song B., Ward B.B. (2008) Anaerobic ammonium oxidation (Anammox) in Chesapeake Bay sediments. Microbial Ecology 55: 311-320.

Richardson J., Williams E.K., Hickey C.W. (2001) Avoidance behaviour of freshwater fish and shrimp exposed to ammonia and low dissolved oxygen separately and in combination. New Zealand Journal of Marine and Freshwater Research 35: 625-633.

Richardson K. (1989) Algal blooms in the North Sea, the good, the bad and the ugly. Journal of Fisheries and Marine Research 8: 83-94.

Richardson K. (1997) Harmful or exceptional phytoplankton blooms in the marine ecosystem. Advances in Marine Biology 31: 301-385.

Richardson K., Beardall J., Raven J.A. (1983) Adaptation of unicellular algae to irradiance- an analysis of strategies. New Phytologist 93: 157-191.

Rolinski S. (1999) On the dynamics of suspended matter transport in the tidal river Elbe: Description and results of a Lagrangian model. Journal of Geophysical Research 104: 26.043-26.057.

Rolinski S., Eichweber G. (2000) Deformations of the tidal wave in the Elbe estuary and their effect on suspended particulate matter dynamics. Physical Chemistry of the Earth 25: 355-358.

Roman C.T., Daiber F.C. (1989) Organic carbon flux through a Delaware Bay salt marsh: tidal exchange, particle size distribution and storms. Marine Ecology Progress Series 54: 149-156.

Rooth J.E., Stevenson J.C., Cornwell J.C. (2003) Increased sediment accretion rates following invasion by Phragmites australis: the role of litter. Estuaries 26: 475-483.

Ross S.W., Dalton D.A., Kramer S., Christensen B.L. (2001) Physiological (antioxidant) responses of estuarine fishes to variability in dissolved oxygen. Comparative Biochemistry and Physiology 130: 289-303.

Roy L., Leconte R., Brissette F.P., Marche C. (2001) The impact of climate change on seasonal floods of a southern Quebec River Basin. Hydrological Processes 15: 3167-3179.

Rysgaard S., Thastum P., Dalsgaard T., Christensen P.B., Sloth N.P. (1999) Effects of salinity on NH_4^+ adsorption capacity, nitrification, and denitrification in Danish estuarine sediments. Estuaries 22: 21-30.

Salomons W., Schwedhelm E., Schoer J., Knauth H.-D. (1988) Natural tracers to determine the origin of sediments and suspended matter from the Elbe estuary. Water Science and Technology 20: 89-102.

Scavia D., Field J.C., Boesch D.F. (2002) Climate change impacts on US coastal and marine ecosystems. Estuaries 25: 149-164.

Schelske C.L., Stoermer E.F., Conley D.J., Robbins J.A., Glover R.M. (1983) Early eutrophication in the lower Great Lakes: new evidence from biogenic silica in sediments. Science 222: 320-322.

Schirmer M., Schuchardt B. (2001) Assessing the impact of climate change on the Weser estuary region: an interdisciplinary approach. Climate Research 18: 133-140.

Schoellhamer D.H. (2001) Influence of salinity, bottom topography, and tides on locations of estuarine turbidity maxima in northern San Francisco Bay. In: McAnally W.H., Mehta A.J. (Eds) Coastal and estuarine fine sediment transport processes. Elsevier Science, Amsterdam, pp. 343-357.

Schubel J., Carter H.H. (1984) The estuary as a filter for fine grained, suspended sediment. In: Kennedy V.S. (Ed.) The estuary as a filter. Academic Press Inc., New York, pp. 81-105.

Schuchardt B., Haesloop U., Schirmer M. (1993) The tidal freshwater reach of the Weser estuary: Riverine or estuarine? Netherlands Journal of Aquatic Ecology 27: 215-226.

Schuchardt B., Schirmer M. (1991) Phytoplankton maxima in the tidal freshwater reaches of two coastal plain estuaries. Estuarine, Coastal and Shelf Science 32: 187-206.

Sebilo M., Billen G., Mayer B., Billiou D., Grably M., Garnier J., Mariotti A. (2006) Assessing nitrification and denitrification in the Seine river and estuary using chemical and isotopic techniques. Ecosystems 9: 564-577.

Seidl I., Tisdell C.A. (1999) Carrying capacity reconsidered: from Malthus' population theory to cultural carrying capacity. Ecological Economics 31: 395-408.

Seitzinger S.P. (1988) Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnology and Oceanography 33: 702-724.

Seitzinger S.P., Harrison J.A., Böhlke J.K., Bouwman A.F., Lowrance R., Peterson B., Tobias C., Van Drecht G. (2006) Denitrification across landscapes and waterscapes: a synthesis. Ecological Applications 16: 2064-2090.

Seitzinger S.P., Nielsen L.P., Caffrey J., Christensen P.B. (1993) Denitrification measurements in aquatic sediments: a comparison of three methods. Biogeochemistry 23: 147-167.

Seitzinger S.P., Nixon S.W., Pilson M.E.Q. (1984) Denitrification and nitrous oxide production in a coastal marine ecosystem. Limnology and Oceanography 29: 73-83.

Servais P., Garnier J. (2006) Organic carbon and bacterial heterotrophic activity in the maximum turbidity zone of the Seine estuary (France). Aquatic Sciences 68: 78-85.

Seys J., Vincx M., Meire P. (1999) Spatial distribution of Oligochaeta (Clitellata) in the tidal freshwater and brackish parts of the Schelde estuary (Belgium). Hydrobiologia 406: 119-132.

Shepherd D., Burgess D., Jickells T., Andrews J., Cave R., Turner R.K., Aldridge J., Parker E.R., Young E. (2007) Modelling the effects and economics of managed realignment on cycling and storage of nutrients, carbon and sediments in the Blackwater estuary UK. Estuarine, Coastal and Shelf Science 73: 355-367.

Sherman K., Alexander L.M., Gold B.D. (1991) Food chains, yields, models and management of large marine ecosystems. Westview Press, Boulder, 320 pp.

Siebens K. (1997) Methaanemissie uit getijdengebieden van de Zeeschelde. Thesis. Gent University, Faculty of Agricultural and Applied Biological Sciences, 85pp.

Simpson R.L., Good R.E., Walker R., Frasco B.R. (1983) The role of Delaware River freshwater tidal wetlands in the retention of nutrients and heavy metals. Journal of Environmental Quality 12: 41-48.

Sin Y., Wetzel R.L., Anderson I.C. (1999) Spatial and temporal characteristics of nutrient and phytoplankton dynamics in the York River estuary, Virginia: Analysis of long term data. Estuaries 22: 260-275.

Smayda T.J. (1990) Novel and nuisance phytoplankton blooms in the sea: evidence for a global epidemic. In: Granéli E., Sundström B., Edler L., Anderson D.M. (Eds) Toxic marine phytoplankton. Elsevier Science Publishing Co., New York, pp. 29-40.

Smayda T.J. (1997) Bloom dynamics: physiology, behavior, trophic effects. Limnology and Oceanography 42: 1132-1136.

Smith S.V., Swaney D.P., Talaue-McManus L., Bartley J.D., Sandhei P.T., McLaughlin C.J., Dupra V.C., Crossland C.J., Buddemeier R.W., Maxwell B.A., Wulff F. (2003) Humans, hydrology, and the distribution of inorganic nutrient loading to the ocean. Bioscience 53: 235-245.

Sobezak W.V., Cloern J.E., Jassby A.D., Cole B.E., Schraga T.S., Arnsberg A. (2005) Detritus fuels ecosystem metabolism but not metazoan food webs in San Francisco estuary's freshwater delta. Estuaries 28: 124-137.

Soetaert K., Herman P. (1994) One foot in the grave: Zooplankton drift into the Westerschelde estuary (The Netherlands). Marine Ecology Progress Series 105: 19-29.

Soetaert K., Herman P. (1995a) Carbon flows in the Westerschelde estuary (The Netherlands) evaluated by means of an ecosystem model (MOSES). Hydrobiologia 311: 247-266.

Soetaert K., Herman P. (1995b) Nitrogen dynamics in the Westerschelde estuary (SW-Netherlands) estimated by means of an ecosystem model (MOSES). Hydrobiologia 311: 225-246.

Soetaert K., Herman P. (1995c) Estimating estuarine residence times in the Westerschelde (The Netherlands) using a box model with fixed dispersion coefficients. Hydrobiologia 311: 215-224.

Soetaert K., Herman P., Kromkamp J. (1994) Living in the twilight: Estimating net phytoplankton growth in the Westerschelde estuary (The Netherlands) by means of an ecosystem model (MOSES). Journal of Plankton Research 16: 1277-1301.

Soetaert K., Middelburg J.J., Heip C., Meire P., Van Damme S., Maris T. (2006) Long-term change in dissolved inorganic nutrients in the heterotrophic Scheldt estuary (Belgium, the Netherlands). Limnology and Oceanography 51: 409-423.

Soetaert K., Van Rijswijk P. (1993) Spatial and temporal patterns of the zooplankton in the Westerschelde estuary. Marine Ecology Progress Series 97: 47-59.

Spurrier J.D., Kjerfve B. (1988) Estimating the net flux of nutrients between a salt marsh and a tidal creek. Estuaries 11: 10-14.

Stehr G., Bottcher B., Dittberner P., Rath G., Koops H.P. (1995) The ammonia-oxidizing nitrifying population of the river Elbe estuary. FEMS Microbiology Ecology 17: 177-186.

Stier D.J., Crance J.H. (1985) Habitat suitability index models and instream flow suitability curves: American shad. U.S. Fish and Wildlife Service Biological Report 82, 34 pp.

Stillman R.A., West A.D., Goss-Custard J.D., McGrorty S., Frost N.J., Morrisey D.J., Kenny A.J., Drewitt A.L. (2005) Predicting site quality for shorebird communities: a case study on the Humber estuary, UK. Marine Ecology Progress Series 305: 203-217.

Struyf E., Dausse A., Van Damme S., Bal K., Gribsholt B., Boschker H.T.S., Middelburg J.J., Meire P. (2006) Tidal marshes and biogenic silica recycling at the land-sea interface. Limnology and Oceanography 51: 838-846.

Struyf E., Van Damme S., Gribsholt B., Meire P. (2005a) Freshwater marshes as dissolved silica recyclers in an estuarine environment (Schelde estuary, Belgium). Hydrobiologia 540: 69-77.

Struyf E., Van Damme S., Gribsholt B., Middelburg J.J., Meire P. (2005b) Biogenic silica in freshwater marsh sediments and vegetation. Marine Ecology Progress Series 303: 51-60.

Struyf E., Van Damme S., Gribsholt B., Middelburg J.J., Meire P. (2007) *Phragmites australis* and Si recycling in freshwater tidal marshes (Schelde estuary, Belgium). Aquatic Botany 87: 134-140.

Struyf E., Van Damme S., Meire P. (2004) Possible effects of climate change on estuarine nutrient fluxes: a case study in the highly nutrified Schelde estuary (Belgium, The Netherlands). Estuarine, Coastal and Shelf Science 60: 649-661.

Suchaneck T.H. (1994) Temperate coastal marine communities: biodiversity and threats. American Zoologist 34: 100-114.

Svobodova Z., Lloyd R., Machova J., Vykusova B. (1993) Water quality and fish health. EIFAC Technical Paper N° 54, FAO, Rome, 59 pp.

Tackx M.L.M., Billiones R., Hannouti A., Yu H., Van Mieghem R., Daro M.N. (1999) Study of the interaction between water column and intertidal in the Zeeschelde: Partim qualification and quantification of organic material and plankton (in Dutch). Report AMIS DS6.2, Free University of Brussels, Department of Ecology and Systematics, Brussels, 68 pp.

Tackx M.L.M., Herman P.J.M., Gasparini S., Irigoien X., Billiones R., Daro M.H. (2003) Selective feeding of *Eurytemora affinis* (Copepoda, Calanoida) in temperate estuaries: model and field observations. Estuarine Coastal and Shelf Science 56: 305-311.

Temmerman S., Bouma T.J., Govers G., Lauwaet D. (2005) Flow paths of water and sediment in a tidal marsh: Relations with marsh developmental stage and tidal inundation height. Estuaries 28: 338-352.

Temmerman S., Govers G., Meire P., Wartel S. (2003) Modelling long-term tidal marsh growth under changing tidal conditions and suspended sediment concentrations, Scheldt estuary, Belgium. Marine Geology 193: 151-169.

Tobias C.R., Anderson I.C., Canuel E.A., Macko S.A. (2001) Nitrogen cycling through a fringing marsh-aquifer ecotone. Marine Ecology Progress Series 210: 25-39.

Townsend A.R., Howarth R.W., Bazzaz F.A., Booth M.S., Cleveland C.C., Collinge S. K., Dobson A.P., Epstein P.R., Holland E.A., Keeney D.R., Mallin M.A., Rogers C.A., Uncles R.J., Stephens J.A. (1993) The freshwater-saltwater interface and its relationship to the turbidity maximum in the Tamar estuary, United Kingdom. Estuaries 16: 126-141.

Troccaz O., Giraud F., Bertru G., Lefeuvre J.C. (1994) Methodology for studying exchanges between salt marshes and coastal marine waters. Wetlands Ecology and Management 3: 37-48.

Uncles R.J., Stephens J.A. (1997) Dynamics of turbidity in the Tweed estuary. Estuarine, Coastal and Shelf Science 45: 745-758.

Uncles R.J., Stephens J.A., Smith R.E. (2002) The dependence of estuarine turbidity on tidal intrusion length, tidal range and residence time. Continental Shelf Research 22: 1835-1856.

Valiela I., Teal J.M., Volkmann S., Shafer D., Carpenter E.J. (1978) Nutrient and particulate fluxes in a salt marsh ecosystem: tidal exchanges and inputs by precipitation and groundwater. Limnology and Oceanography 23: 798-812.

Van Alsenoy V., Van Put A., Bernard P., Van Grieken R. (1989) Chemical characterization of suspensions and sediments in the North Sea and Scheldt estuary. In: Pichot G. (Ed.), Progress in Belgian oceanographic research. Royal Academy of Sciences, Brussels, pp. 351-368.

Van Beusekom J.E.E., Brockmann U.H. (1998) Transformation of phosphorus in the Elbe estuary. Estuaries 21: 518-526.

Van Beusekom J.E.E., de Jonge V.N.N. (2002) Long-term changes in Wadden-Sea nutrient cycles: Importance of organic matter import from the North Sea. Hydrobiologia 475/476: 185-194.

Van Cappellen P. (2003) Biomineralisation and global biogeochemical cycles. Reviews in Mineralogy and Geochemistry 54: 357-381.

Van Cleve F.B., Leschine T., Klinger T., Simenstad C. (2006) An evaluation of the influence of natural science in regional-scale restoration projects. Environmental Management 37: 367-379.

Van Damme S., Dehairs F., Tackx M., Beauchard O., Struyf E., Gribsholt B., Van Cleemput O., Meire P. (2009) Tidal exchange between a freshwater tidal marsh and an impacted estuary: the Scheldt estuary, Belgium. Estuarine, Coastal and Shelf Science 85: 197-207.

Van Damme S., Meire P., Maeckelberghe H., Verdievel M., Bourgoing L., Taverniers E., Ysebaert T., Wattel G. (1995) De waterkwaliteit van de Zeeschelde: evolutie in de voorbije dertig jaar. Water 85: 244-256.

Van Damme S., Struyf E., Maris T., Meire P. (2009) Characteristic aspects of the tidal freshwater zone that affect aquatic primary production. In: Barendregt A., Whigham D.F., Baldwin A.H. (Eds) Tidal freshwater wetlands. Backhuys Publishers, Leiden, The Netherlands, pp. 123-136.

Van Damme S., Struyf E., Maris T., Ysebaert T., Dehairs F., Tackx M., Heip C., Meire P. (2005) Spatial and temporal patterns of water quality along the estuarine salinity gradient of the Scheldt estuary (Belgium and The Netherlands): results of an integrated monitoring approach. Hydrobiologia 540: 29-45.

Van de Koppel J., Van der Wal D., Bakker J.P., Herman P.M.J. (2005) Self organization and vegetation collapse in salt marsh ecosystems. American Naturalist 165: 1-12.

Vanderborght J.-P., Wollast R., Billen G. (1977) Kinetic-models of diagenesis in disturbed sediments .1. Mass-transfer properties and silica diagenesis. Limnology and Oceanography 22: 787-793.

Vanderborght J.-P., Wollast R., Loijens M., Regnier P. (2002) Application of a transport-reaction model to the estimation of biogas fluxes in the scheldt estuary. Biogeochemistry 59: 207-237.

Van der Nat J.F., Middelburg J.J. (2000) Methane emission from tidal freshwater marshes. Biogeochemistry 49: 103-121.

Van der Spek A.J.F. (1997) Tidal asymmetry and long-term evolution of Holocene tidal basins in the Netherlands: simulations of paleo-tides in the Schelde estuary. Marine Geology 141: 71-90.

Vanderweijden C.H., Middelburg J.J. (1989) Hydrogeochemistry of the river Rhine - long-term and seasonal variability, elemental budgets, base levels and pollution. Water Research 23: 1247-1266.

Van der Zee C., Roevros N., Chou L. (2007) Phosphorus speciation, transformation and retention in the Scheldt estuary (Belgium/The Netherlands) from the freshwater tidal limits to the North Sea. Marine Chemistry 106: 76-91.

Van Eck G.T.M., De Rooij N.M. (1993) Potential chemical time bombs in the Schelde estuary. Land Degradation and Rehabilitation 4: 317-332.

Van Oost K., Govers G., Desmet P. (2000) Evaluating the effects of changes in landscape structure on soil erosion by water and tillage. Landscape Ecology 15: 597-591.

Van Rompaey A.J.J., Verstraeten G., Van Oost K., Govers G., Poesen J. (2001) Modelling mean annual sediment yield using a distributed approach. Earth Surface Processes and Landforms 26: 1221-1236.

Van Spaendonk J.C.M., Kromkamp J.C., De Visscher P.R.M. (1993) Primary production in a turbid coastal plain estuary, the Westerschelde (The Netherlands). Netherlands Journal of Sea Research 31: 267-279.

Venice System (1958) Symposium on the classification of brackish waters, Venice April 8-14, 1958. Archives of Oceanography and Limnology 11: 1-248.

Verity P.G. (2002) A decade of change in the Skidaway River Estuary. I. Hydrography and nutrients. Estuaries 25: 944-960.

Vörösmarty C.J., Peterson B.J. (2000) Macro-scale models of water and nutrient flux to the coastal zone. In Hobbie J.E. (Ed.) Estuarine science. Island Press, Washington D.C., 539 pp.

Wang B. (2006) Cultural eutrophication in the Changjiang (Yangtze River) plume: History and perspective. Estuarine, Coastal and Shelf Science 69: 471-477.

Wang Z.B., Jeuken M.C.J..L, Gerritsen H., De Vriend H.J., Kornman B.A. (2002) Morphology and asymmetry of the vertical tide in the Westerschelde estuary. Continental Shelf Science 22: 2599-2609.

Wanielista M.P. (1990) Hydrology and water quantity control. John Wiley & Sons, New York, 565 pp.

Wannamaker C.M., Rice J.A. (2000) Effects of hypoxia on movements and behavior of selected estuarine organisms from the southeastern United States. Journal of Experimental Marine Biology and Ecology 249: 145-163.

Wayne P., Wolfe A.H. (2003) Human health effects of a changing global nitrogen cycle. Frontiers in Ecology and the Environment 1: 240-246.

Weir D.J., McManus J. (1987) The role of wind in generating turbidity maxima in the Tay estuary. Continental Shelf Research 7: 1315-1318.

Werritty A. (2002) Living with uncertainty: climate change, river flows and water resource management in Scotland. Science of the Total Environment 294: 29-40.

Weston N.B., Dixon R.E., Joye S.B. (2006) Ramifications of increased salinity in tidal freshwater sediments: Geochemistry and microbial pathways of organic matter mineralization. Journal of Geophysical Research-Biogeosciences 111: Art. No. G01009 FEB 7 2006.

Whiting G.J., Childers D.L. (1989) Subtidal advective water flux as a potentially important nutrient input to Southeastern U.S.A. saltmarsh estuaries. Estuarine, Coastal and Shelf Science 28: 417-431.

Whiting, G.J., Mc Kellar Jr., Spurrier J.D., Wolaver T.G. (1989) Nitrogen exchange between a portion of vegetated salt marsh and the adjoining creek. Limnology and Oceanography 34: 463-473.

Wigley T.M.L., Raper S.C.B. (1992) Implications for climate and sea-level of revised IPCC emissions scenarios. Nature 357: 293-300.

Winterwerp J.C., Manning A.J., Martens C., De Mulder T., Vanlede J. (2006) A heuristic formula for turbulence-induced flocculation of cohesive sediment. Estuarine, Coastal and Shelf Science 68: 195-207.

Wolff W.J. (1973) The estuary as a habitat. An analysis of data on the soft-bottom macrofauna of the estuarine area of the Rivers Rhine, Meuse and Scheldt. Zoologische Verhandelingen, Leiden, 242 pp.

Wollast R. (1978) Modelling of biological and chemical processes in the Scheldt estuary. In Nihoul J.C.D. (Ed.) Hydrodynamics of Estuaries and Fjords. Elsevier, Amsterdam, pp. 63-77.

Wollast R. (1982) Behaviour of organic carbon, nitrogen and phosphorous in the Scheldt estuary. Thalassia Yugoslavica 18: 11-34.

Wollast R. (1988) The Scheldt Estuary. In: Salomons W., Bayne W.L., Duursma E.K. Forstner U. (Eds) Pollution of the North Sea: An assessment. Springer-Verlag, Berlin, pp. 183-193.

Wright S.W., Jeffrey S.W., Mantoura R.F.C., Llewellyn C.A., Bjornland T., Repeat D., Welshmeyer N. (1991) Improved HPLC method for the analysis of chlorophylls and carotenoids from marine phytoplankton. Marine Ecology Progress Series 77: 183-196.

Yamada S.S., D' Elia C.F. (1984) Silicic-acid regeneration from estuarine sediment cores. Marine Ecology Progress Series 18: 113-118.

Yozzo D.J., Clark R., Curwen N., Graybill M.R., Reid P., Rogal K., Scanes S., Tilbrook C. (2000) Managed retreat: assessing the role of the human community in habitat restoration projects in the United Kingdom. Ecological Restoration 18: 234-244.

Ysebaert T., De Neve L., Meire P. (2000) The subtidal macrobenthos in the mesohaline part of the Schelde Estuary (Belgium): influenced by man? Journal of the Marine Biological Association of the United Kingdom 80: 587-597.

Ysebaert T., Fettweis M., Meire P., Sas M. (2005) Benthic variability in intertidal soft-sediments in the mesohaline part of the Schelde estuary. Hydrobiologia 540: 197-216.

Ysebaert T., Herman P.M.J., Meire P., Craeymeersch J., Verbeek H., Heip C.H.R. (2003) Large-scale spatial patterns in estuaries: estuarine macrobenthic communities in the Scheldt estuary, NW-Europe. Estuarine, Coastal and Shelf Science 57: 335-355.

Ysebaert T., Meire P., Maes D., Buijs J. (1993) The benthic macrofauna along the estuarine gradient of the schelde estuary. Netherlands Journal of Aquatic Ecology 27: 327-341.

Zwolsman J.J.G. (1994) Seasonal variability and biogeochemistry of phosphorus in the Scheldt estuary, South-West Netherlands. Estuarine, Coastal and Shelf Science 39: 227-248.

Zwolsman J.J.G. (1999) Present-day trace metal geochemistry in the Scheldt estuary. In: Zwolsman J.J.G. (Ed.) Geochemistry of trace metals in the Scheldt estuary. Geologica Ultraiectina 171: 151-1.

www.upa-editions.be

ISBN 978 90 5487 760 8